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Pyrolysis Analysis of the Herbicide Paraquat on *Cannabis* by Coupled Gas Chromatography-Infrared Spectroscopy

The recent furor over paraquat contamination of Mexican marijuana imported into this country has involved some controversy over how much of the herbicide survives pyrolysis in marijuana cigarettes and how much danger the unknown amount of paraquat poses to the *Cannabis* smoker [*1–5*]. While much is known about the pulmonary toxicity of ingested paraquat [*6–9*], little is known about the toxicity of inhaled paraquat, and even less about the physiological activity of its pyrolysis products.

We have studied the pyrolysis of paraquat both by itself and in contaminated marijuana with an eye toward determining the temperature at which it is converted to its well-known pyrolysis product, 4,4′-dipyridyl [*10*]. We wished to confirm the extent of this conversion and to see if any other compounds might be produced.

The availability of a relatively new technique, the combination of gas chromatography and infrared spectroscopy for positive identification of the chromatographic peaks, provided the opportunity to carry out pyrolysis experiments.

Experimental Methods and Materials

Authentic, paraquat-contaminated marijuana was supplied by Dr. Carlton Turner of the University of Mississippi. His analysis of the two samples showed contamination at two levels: 12.51 and 99.53 ppm. Most seized, contaminated marijuana falls within this range of concentrations. Higher level contamination was achieved by evaporating standard paraquat (courtesy Ortho Division of Chevron Chemical Co.) onto uncontaminated marijuana. Standard 4,4′-dipyridyl dihydrate was obtained from Aldrich Chemical Co.

The instrument used for the pyrolysis analysis was the Sadtler CIRA 101 chromatographic infrared analyzer, mated to a Beckmann Acculab 2 infrared spectrophotometer. A Chemical Data Systems 120 Pyroprobe was fitted onto the gas chromatograph's inlet port. The gas chromatographic procedure was adapted from the technique of Cannard and Criddle [*11*].

Several experiments were performed. The retention time and gas-phase infrared spectrum for standard 4,4′-dipyridyl were first established. A graph of retention time versus sample size was prepared so that overloading effects could be accounted for. Paraquat dichloride was then pyrolyzed in milligram quantities to get spectra of the peaks produced under different pyrolysis temperatures and times.

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Next, conversion experiments were run in which the paraquat was pyrolyzed at the experimental temperature: after the peaks had eluted, the same sample was again pyrolyzed at the highest temperature available (1100°C) to convert the remaining paraquat completely to decomposition products. The ratio of the areas of the pyrolysis peaks was used to compute the percentage of conversion. Smaller amounts (0.1 mg) of paraquat were used here because pyrolysis was less efficient when larger samples were used. Contaminated marijuana would be expected to contain even smaller amounts of paraquat than this.

Contaminated marijuana was similarly pyrolyzed to see if the dipyridyl peak could be seen among the other pyrolysis products.

Finally the whole experiment was repeated with a different column to ensure that the peaks with the first column were due to only one component each.

The operating conditions for the CIRA and accessories under which the experiment was performed are given in Table 1. The finely powdered sample was loaded in the coil Pyroprobe by means of 25- by 2-mm inside diameter quartz tubes.

When peaks were scanned with the spectrometer the flow to the column was stopped. This is possible with the CIRA analyzer without the retention times or peak shape being affected [*12,13*].

Peak areas on chromatograms were measured by multiplying peak height by peak half-height width.

Results and Discussion

Pyrolysis of paraquat at all temperatures studied gave only two peaks: one which was essentially not retained on the column, and one which was retained for several minutes, depending on the temperature and column (Fig. 1). Stop-flow examination of the first peak showed it to be identical in spectrum to standard gas-phase spectra of chloromethane (CH_3Cl) (Fig. 2). The second peak gave a spectrum identical to that of authentic 4,4′-dipyridyl (Fig. 3).

TABLE 1—*Operating conditions for the CIRA and accessories.*

CDS-120 Pyroprobe accessory	
Function	run
Interface	off
Ramp	off
Interval, s	10
Final temperature, °C	500 to 1100
CIRA 101 analyzer	
Mode of operation	low pressure
Column	[a] 0.5-m by 6-mm outside diameter glass tubing packed with 10% CW-20M on Chromosorb GHP, 80-100 mesh previously treated with 2% sodium hydroxide [b] 2-m by 6-mm outside diameter glass tubing packed with 3% OV-17 on Chromosorb 750, 100-120 mesh
Carrier gas, helium, ml/min	40
Column head pressure, kPa (psig)	34 (5)
Column bottom pressure, psig	0
Injection port temperature, °C	240
Thermal conductivity detector temperature, °C	260
Optical cell temperature, °C	260
Column oven temperature, °C	[a] isothermal, 220 [b] isothermal, 190
Infrared spectrometer (Acculab 4)	
Operation mode	fast scan (3 min)

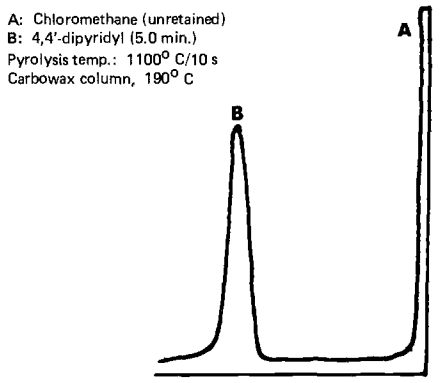

FIG. 1—*Gas chromatographic separation of paraquat pyrolysis products.*

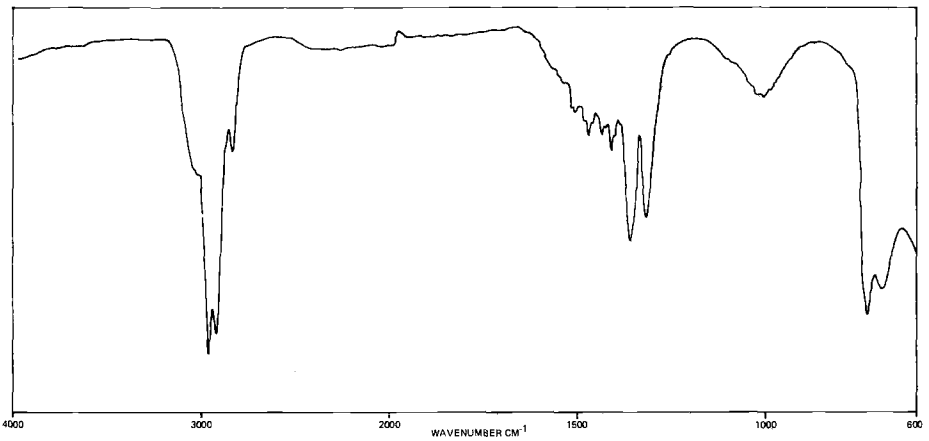

FIG. 2—*Gas-phase infrared spectrum of Peak A (chloromethane).*

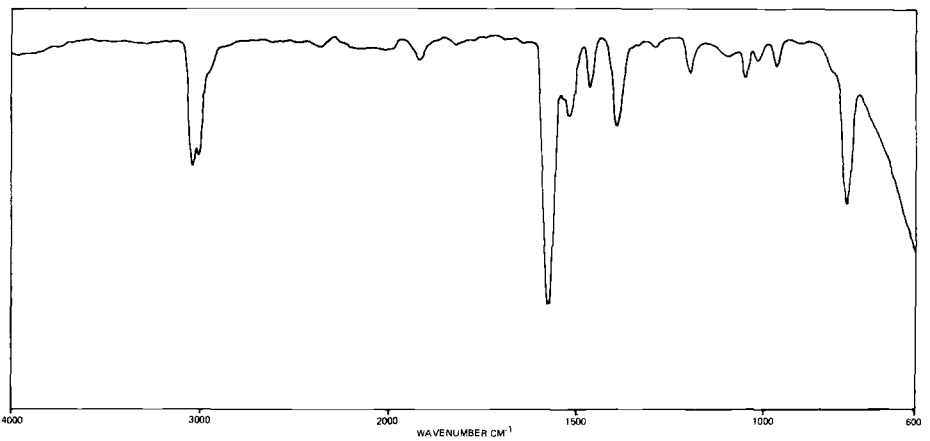

FIG. 3—*Gas-phase infrared spectrum of Peak B (4,4'-dipyridyl).*

Weighing the pyrolysis tube before and after pyrolysis, then flaming the tube in air to remove the slight blackish residue, showed that at 1100°C only 4.4% of a 13-mg sample of paraquat dichloride failed to get onto the column. Thus the peaks we see represent nearly all of the pyrolysis products.

Since the carrier gas was helium, one might argue that the experiment should be run with air as part of the carrier gas. Apart from the difficulties this would cause with the detector filaments, an oxidizing environment is unnecessary, since Chopra and Sherman [*14*] have reported that, for tobacco, the burning zone is reducing in nature.

Even at high gain, no peaks other than the two mentioned above were seen on the chromatograms of standard paraquat pyrolysis.

The temperature of conversion with small amounts of paraquat being used to approximate the trace levels found in contaminated samples showed that the pyrolysis occurs essentially completely in 10 s at no more than 650°C. With very small amounts it was possible to narrow the partial conversion range to between 600 and 610°C. In the real-life situation heat transfer and surface area factors, which cut down efficient pyrolysis of paraquat in mass, become negligible compared to the thermodynamics, so we feel safe in saying that once 610°C is reached all paraquat will be converted to dipyridyl and chloromethane within 10 s.

Workers on tobacco pyrolysis [*15*] have measured peak temperatures in the burning zone of cigarettes and found them to be as high as 900°C. Thus extrapolation to the combustion of marijuana in cigarettes argues for the complete conversion of paraquat.

When *Cannabis* was pyrolyzed, we were able to distinguish the dipyridyl peak from the rest of the chromatogram (Fig. 4) at very high levels of spiking (5%). We did not expect to detect paraquat pyrolysis at the lower levels since the CIRA is not designed for high sensitivity of detection. At 5% contamination the dipyridyl peak was clearly visible, and at 1% it was still seen above the tailing baseline. At 100 ppm it was merely a small, almost flat peak. The *Cannabis* leaf constituents themselves destructively pyrolyze and these are responsible for the large tailing peak at the front of the chromatogram.

Since the OV-17 column has been widely used to separate cannabinoids, it might be expected that cannabinoid peaks would interfere. Pyrolysis of standard cannabinoids gave no peaks save the unretained one characteristic of uncontaminated *Cannabis*. The cannabinoids are presumably destroyed in the metal injector port on pyrolysis, so that none of the typical peaks seen at normal temperatures with ordinary gas chromatography appear. It might be noted that studies have been carried out by Agurell and Leander [*16*] on the

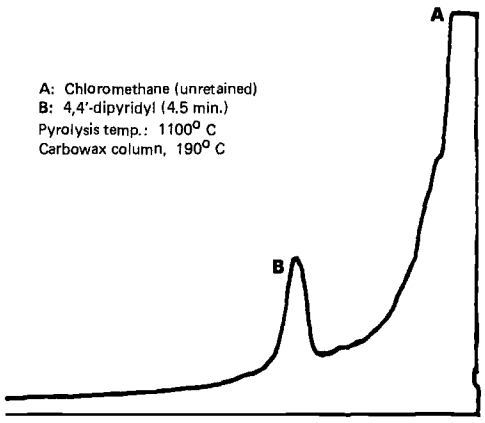

FIG. 4—*Pyrogram of 5% paraquat-contaminated marijuana.*

stability of cannabinoids under smoking conditions and that they have observed that approximately 20% of the cannabinoids survive the smoking zone intact at the lower temperature conditions of smoking.

Chopra and Sherman [*14*] have shown chloromethane to be a normal constituent of tobacco smoke. In work aimed at determining the effects of dichloro-diphenyl-trichloroethane (DDT) pyrolysis with tobacco, the amount of chloromethane generated by the tobacco far exceeded that generated by the DDT. It seems safe to assume that the pyrolysis of marijuana likewise produces chloromethane at higher levels than does the pyrolysis of paraquat. In fact, measurement of the spectrum of the unretained peak indicates that it is largely chloromethane. Toxic effects of chloromethane [*17*] should be similar for both paraquat-contaminated and uncontaminated marijuana.

The other product, 4,4′-dipyridyl, has not been evaluated for its toxicity [*10*]. The 2,2′-isomer is known to occur in tobacco smoke [*18*] and has been pharmacologically evaluated [*19*], but the 4,4′- isomer has not been studied.

We would suggest that an evaluation of 4,4′-dipyridyl toxicity be carried out by using inhalation of volatilized dipyridyl. From our results it would seem certain that this compound occurs at much higher levels than paraquat in paraquat-contaminated marijuana smoke. Even allowing for paraquat's undoubtedly higher toxicity, the production of 4,4′-dipyridyl is cause for concern, since in this study we have confirmed its presence under controlled pyrolysis conditions.

Summary

Pyrolysis gas chromatography coupled with infrared identification of eluted peaks confirms that paraquat is pyrolyzed into chloromethane and 4,4′-dipyridyl at smoking temperatures and above. This reaction occurs at 610°C to completion in small amounts in an inert atmosphere. The toxicity of 4,4′-dipyridyl remains to be determined. Pyrolysis of contaminated marijuana also produces the same two products, although detection at low limits is difficult with this procedure.

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