Table I. Phthalate Ester Residues (ppb) in Fish Available to the Canadian Consumer

Sample	DEHP	DBP
Unprocessed fish		
Eel	104[b]	—
Catfish (L. St. Pierre)	+[a]	—
Pickerel (L. Huron)	+	—
Pickerel (L. Ontario)	+	+[a]
Pickerel (L. Ontario)	+	+
Pickerel (L. Ontario)	—	+
Processed canned fish		
Tuna	40	—
Tuna	160[b]	78[b]
Tuna	140[b]	+
Salmon	63	+
Salmon	89	37
Sardine	—	—
Crab	—	—
Shrimp	—	+
Baby clams	—	—
Processed frozen fish		
Rainbow trout	+	—
Ocean perch	+	—
Mackerel	+	—
Sole	—	—
Oyster	—	—
Scallop	—	—

[a] Levels less than twice background. [b] Confirmed by glc–mass spectrometry.

and a background level is always found in analysis of "blank" samples (*Chem. Eng. News*, 1971; Williams, 1973). For a 100-g fish sample analyzed by the above method, the background levels were approximately 15 ppb for DEHP and 10 ppb for DBP. Levels of DEHP and DBP of less than twice background are designated as trace amounts in Table I; other values have been corrected for background. The identification of phthalate esters by glc has been extensively reviewed (Bloom, 1972; Fishbein and Albro, 1972). Confirmation by glc–mass spectrometry is simple at the 1-ppm level but due to background interference is difficult at lower levels (Williams, 1973). Phthalate esters at levels greater than five times the background level were confirmed by glc–mass spectrometry but lower levels of phthalate esters were only confirmed by analysis on two glc columns.

Stalling *et al.* (1973) have recently reported that DEHP and DBP are metabolized by fish and it would appear that high residue levels would be expected only in those fish continuously exposed to phthalate esters. Highest levels of phthalate esters have been reported in fish from waters adjacent to industrial areas and in hatchery fish fed diets contaminated with phthalate esters (Mayer *et al.*, 1972; Zitko, 1972).

LITERATURE CITED

Bloom, P. J., *J. Chromatogr.* **72**, 35 (1972).
Chem. Eng. News, **49**(45), 8 (1971).
Corcoran, E. F., *Environ. Health Perspect.* 1(3), 13 (1973).
Fishbein, L., Albro, P. W., *J. Chromatogr.* **70**, 365 (1972).
Hites, R. A., *Environ. Health Perspect.* 1(3), 17 (1973).
Mayer, F. L., Stalling, D. L., Johnson, J. L., *Nature (London)* **238**, 411 (1972).
Stalling, D. L., Hogan, J. W., Johnson, J. L., *Environ. Health Perspect.* 1(3), 159 (1973).
Tepper, L. B., *Environ. Health Perspect.* 1(3), 179 (1973).
Williams, D. T., *J. Ass. Offic. Anal. Chem.* **56**, 181 (1973).
Zitko, V., Technical Report No. 344, Fisheries Research Board of Canada (1972).

David T. Williams

Food Research Laboratories
Health Protection Branch
Tunney's Pasture
Ottawa, K1A 0L2, Canada

Received for review May 23, 1973. Accepted August 21, 1973.

Long-Chain Hydrocarbons of *Cannabis* and Its Smoke

A series of long-chain paraffins has been identified in *Cannabis* and its smoke by gas chromatography and mass spectrometry. The level of hydrocarbons was determined to be about half that found in tobacco and its smoke, although the effect of smoking on the paraffins in the *Cannabis* plant material was comparable to analogous studies of tobacco and its smoke.

Many studies have been published concerning the cannabinoids in *Cannabis* (Gaoni and Mechoulam, 1971) but only one report has been found on those compounds present in the smoke condensate. Recently, Fentiman *et al.* (1973) reported the identification of several noncannabinoid phenols present in the smoke condensate of *Cannabis* using gas chromatography–mass spectrometry (gc–ms) techniques. As an extension of this work, we now wish to report the identification and comparison of the hydrocarbons present in the plant extract and those transferred and/or generated during the smoking process.

EXPERIMENTAL SECTION

The *Cannabis* used in this study (strain MS-13) was cultivated by a standard method (Doorenbos *et al.*, 1971) and known weights were extracted with 95% ethanol (Groce and Jones, 1973). The ethanol was concentrated and diluted with water, and the mixture was exhaustively extracted with hexane. After concentration, the hexane solution was made to volume and aliquots were used for analysis. These were chemically separated into basic, acidic, and neutral fractions and the neutral solution was concentrated to a thick syrup. This was chromatographed on silicic acid and initial waxy fractions were eluted with hexane. Treatment with urea in hot methanol formed an adduct which was washed with hexane and decomposed with water and extraction with hexane gave a clean mixture of long-chain hydrocarbons (Johnston and Jones, 1968). Separation of the straight-chain paraffins from those with branching was affected with Linde 5A molecular seives.

For smoke analysis, 70-mm cigarettes were hand rolled and smoked on a smoking machine taking a 40-ml puff of 2 sec duration every minute. The average weight per ciga-

Table I. Hydrocarbons of Plant Extract

Carbon number	Assignment[a]	Retention time	Weight[b] %
22	S	5.38	0.83
23	S	6.37	0.65
24	S	7.45	0.36
25	*iso*	8.08	0.57
25	S	8.58	2.79
26	*anteiso*	9.41	2.26
26	S	9.75	0.76
27	*iso*	10.44	0.56
27	S	10.96	15.08
28	*anteiso*	11.81	1.45
28	S	12.51	3.06
29	*iso*	12.87	0.49
29	S	13.42	55.27
30	*anteiso*	14.18	6.48
30	S	14.48	2.80
31	S	15.63	6.59

[a] S, straight-chain paraffin; *iso*, isoparaffin; *anteiso*, anteisoparaffin. [b] The peaks were normalized assuming that the relative molar response of homologs is linear with respect to carbon number.

Table II. Hydrocarbons of Smoke Condensate

Carbon number	Assignment[a]	Retention time	Weight[b] %
17	S	4.29	1.20
19	U_1	4.50	1.49
18	S	5.18	2.11
20	U_1	5.72	0.11[c]
20	U_2	5.72	4.30
19	S	6.16	4.18
21	U_2	6.52	0.70
20	S	7.07	4.52
21	U_2	7.07	0.40[c]
21	S	7.98	4.22
22	S	8.89	4.38
25	BU_2	8.89	1.24[c]
23	S	9.68	5.11
24	S	10.53	3.99
25	*iso*	10.95	1.19
25	S	11.33	4.03
26	*anteiso*	11.87	1.32
26	S	12.12	3.14
27	*iso*	12.52	0.77
27	S	12.93	5.77
28	*anteiso*	13.38	0.73
28	S	13.60	3.46
29	*iso*	14.02	0.50
29	S	14.59	18.21
30	*anteiso*	14.84	1.43
30	S	15.03	3.57
31	S	15.73	5.56
UK[d]		16.13	3.42
M^+ 398	U_5	16.73	3.20
UK[d]		16.96	2.49
M^+ 408	U_7	17.39	3.31

[a] S, straight-chain paraffin; U, unsaturated straight-chain hydrocarbon; BU, branched unsaturated hydrocarbon; x, degree of unsaturation; *iso*, isoparaffin; *anteiso*, anteisoparaffin; M^+, molecular ion. [b] The peaks were normalized assuming that the relative molar response of homologs is linear with respect to carbon number. [c] Estimation of percentage of peak shoulder identified by gc–ms but not resolved into two peaks upon integration of the chromatogram. [d] UK, unknown.

rette was 0.9 g. The smoke condensate was trapped at Dry Ice–isopropyl alcohol temperature and removed from the trap by washing with methylene chloride. This was made to volume and aliquots were taken for analysis. The sample preparation was the same as that described above. All fractions were analyzed by gas chromatography (gc) and gas chromatography–mass spectrometry (gc–ms).

A Beckman GC-4 equipped with a flame ionization detector and a 10 ft × ⅛ in. column of 2% OV-17 on Gas Chrom Q was used. The inlet and detector were maintained at 350° and the helium flow was 26 ml/min. For the plant hydrocarbons, the runs were programmed from 200° to 280° at 5°/min, while for smoke condensate hydrocarbons, the program was from 150° to 310° at 10°/min. Areas were determined by a Hewlett-Packard 3370 digital integrator. For the gc–ms analysis, the sample was injected onto a 9 ft × ¼ in. glass column packed with 1% OV-17 on Chromosorb W, which was programmed from 150° to 240° at 5°/min. The LKB 9000 instrument was operated at an ionizing voltage of 20 eV, with the separator at 260° and the ion source at 270°.

The results are shown in Tables I and II.

RESULTS AND DISCUSSION

An examination of Table I reveals an expected pattern (Eglinton and Hamilton 1967); the paraffin constituents of plant waxes are mixtures of long-chain hydrocarbons, with the odd-carbon paraffins predominating over the even-numbered and branched paraffins. The straight-chain hydrocarbons comprise 88.2% of the paraffin wax, which is characterized by the predominance of nonacosane (55.27%). The other 11.8% of the paraffins are those with methyl branching at the 2 (*iso*) and 3 (*anteiso*) positions.

The smoke condensate contains all the paraffins (Table II) identified in the plant material, along with several others that presumably resulted from the pyrolytic cracking of the higher straight-chain homologs. Interestingly, there are no additional branched paraffins. Preferential cracking of the *iso* and *anteiso* paraffins at the branched position, analogous to that observed in their mass spectral fragmentation (Mold *et al.*, 1963), could account for this phenomenon. Unlike the composition of the plant waxes, those of the smoke condensate contain unsaturated hydrocarbons. These could result from the pyrolytic cracking process accompanied by the abstraction of hydrogen. Two hydrocarbons that are not present in the plant extract are those eluting after hentriacontane (C_{31}). The mass spectral fragmentation patterns of these compounds indicate that they consist of long-chain moieties attached to an unsaturated and probably aromatic system. These compounds could arise from the recombination of cleavage products by pyrolytic synthesis.

A comparison of the composition of the plant extract and smoke condensate of *Cannabis* shows that nonacosane is the major component of both mixtures, although its relative percentage is three times greater in the plant extract. Furthermore, the percentages of all the hydrocarbons present in the smoke condensate other than 3-methylnonacosane have increased significantly relative to nonacosane. This effect, due to pyrolytic cracking, has also been observed in the comparison of the hydrocarbons of tobacco (Mold *et al.*, 1963; Spears *et al.*, 1963) and its smoke, although the effect is greatly pronounced in the hydrocarbons of *Cannabis* smoke.

Although our study was not as comprehensive as the numerous reports concerning tobacco (for example, see Stedman, 1968) our findings parallel the comparable results obtained with tobacco. It would not seem unreasonable to suggest that a significant similarity exists between tobacco and marihuana with respect to the hydrocarbons and their pyrolysis products.

ACKNOWLEDGMENT

We thank James M. Taylor and Charles S. Fenski of the Research Triangle Institute, Research Triangle Park,

N. C., for providing the combined gc–ms data. We also thank Doris B. Sartain for technical assistance.

LITERATURE CITED

Doorenbos, N. J., Fetterman, P. S., Quinby, N. W. Turner, C. E., *Ann. N. Y. Acad. Sci.* **191**, 3 (1971).
Eglinton, G., Hamilton, R. J., *Science* **156**, 1322 (1967).
Fentiman, A. F., Foltz, R. L., Kinger, G. W., *Anal. Chem.* **45**, 580 (1973).
Gaoni, Y., Mechoulam, R., *J. Amer. Chem. Soc.* **93**, 217 (1971).
Groce, J. W., Jones, L. A., *J. Agr. Food Chem.* **21**, 211 (1973).
Johnston, R. L., Jones, L. A., *Anal. Chem.* **40**, 1728 (1968).
Mold, J. E., Stevens, R. K., Means, R. E., Ruth, J. M., *Biochemistry* **2**, 605 (1963).
Spears, A. W., Lassiter, C. W., Bell, J. H., *J. Gas Chromatogr.* April, 34 (1963).
Stedman, R. L., *Chem. Rev.* **68**, 153 (1968).

Theodore C. Adams, Jr.
Louis A. Jones*

Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27607

Received for review March 21, 1973. Accepted July 13, 1973. This work was supported by Grant MH 17430-03 from the National Institute of Health.

Corrections

CONTROLLED RELEASE FERTILIZERS BY CHEMICAL MODIFICATION OF UREA: TRIURET

In this article by John T. Hays and William B. Hewson [*J. Agr. Food Chem.* **21**(3), 498 (1973)], in the sixth line of the second full paragraph, first column of page 499, the word "ureidomethylenehydrotriazinedione" should read "hydrotriazinedione."

THE BIOCHEMISTRY OF TEA FERMENTATION: OXIDATIVE DEGALLATION AND EPIMERIZATION OF THE TEA FLAVANOL GALLATES

In this article by Philip Coggon, Gerald A. Moss, Harold N. Graham, and Gary W. Sanderson [*J. Agr. Food Chem.* **21**(4), 727 (1973)], on page 729, the last sentence of the paragraph which finishes at the top of column 2 should be deleted and replaced by the following sentence: "It remained for Takino and Imagawa (1964) to establish that theaflavin was formed by the cooxidation of II and IV."

MICRODETERMINATION OF CHLORO-*s*-TRIAZINES IN SOIL BY GAS–LIQUID CHROMATOGRAPHY WITH NICKEL ELECTRON CAPTURE OR ELECTROLYTIC CONDUCTIVITY DETECTION

In this article by Hong Y. Young and Ada Chu [*J. Agr. Food Chem.* **21**(4), 711 (1973)], the end of one sentence and the beginning of another were omitted from the text. The second sentence of the first full paragraph, second column, page 713, should read as follows: "Decreased sensitivity is usually corrected for by following the prescribed directions for changing the strontium hydroxide scrubber, checking water quality, or reconditioning the nickel catalyst by treatment with oxygen followed by hydrogen. Soaking the quartz tube containing the catalyst in 6 *N* nitric acid until a faint green color was apparent in the acid was helpful in restoring the activity of the catalyst."