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Pesticide Residues in Edible Oils And Oil Seeds

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Oils and fats are vitally important for our food, bodily massage and cosmetics. In view of the acute shortage of edible oils in India, a crash programme has been initiated to increase production of different kind of edible oils to fill the gap between production and demand. Pesticides are used on large scale in crop cultivation, to control pest and to raise crop yield. Reports have shown that some of oils and oilseeds available commercially, are contaminated with pesticides (Thakare et al. 1969, Srivastava et al. 1983 and Dikshith et al. 1987). However no clear cut correlations have been established between the pesticide residues in edible oils and deleterious effects in organisms. As a first step an attempt has been made to quantify residues of different organochlorine pesticides in major varieties of edible oils and oil seeds used in this country.

MATERIALS AND METHODS

Analytical standards for organochlorine pesticides were obtained from U.S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository (MD-8), Research Triangle Park, NC, USA. All solvents used in extraction and cleanup process were of A.R. Grade and distilled in all glass-still prior to use. Florisil (Fluka A.G.) activated charcoal (E. Merck India Ltd.), Sodium sulfate anhydrous (Sarabhai Chemical, Bombay) used in this experiment, were of high purity. A total of sixty samples of six commonly available edible oils and oil seeds such as groundnut (peanut), seasame (white dehusked), mustard, coconut and hydrogenated vegetable oils were procured from the market of

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Lucknow, Uttar Pradesh, India. The following modified methods of Mills (AOAC 1984) for the extraction and cleanup of all the samples was used:

Each samples of oil seeds taken in triplicate was weighed (25 g), blended for 3 min with 150 ml CH_3CN in high speed homogenizer. The macerate was filtered with suction through Buchner funnel. The generation head and jar was washed with 25 ml CH_3CN. The filtrate transferred to 1L separatory funnel. 450 mL water containing 4% $Na_2SO_4$was added to the separatory funnel and shaken vigorously for 3 min. Extraction was carried out successfully with 100, 50 and 50 mL portions of hexane, shaking each time for 3 min. The extracts were filtered through 30 g anhydrous Na_2SO_4 under high pressure. The Na_2SO_4 layer was rinsed with additional 20 mL n-hexane. The combined hexane extractes were evaporated to dryness with vaccum rotary evaporator at 35°C. The extract was dissolved in 25 mL distilled CH_3CN and washed with 4% Na_2SO_4 and re-extracted with 25 mL hexane fraction was filtered through 30 g anhydrous Na_2SO_4 layer. The Na_2SO_4 layer was washed again with 10 mL portion of hexane. The combined hexane extract was concentrated to 1 mL volume.The mixed phase column was dry packed with 1 x 5 cm bed of anhnydrous Na_2SO_4 layer at the bottom followed by 1 x 10 cm bed of 2% deactiavated Florisil (Fluka A.G.), 1 x 10 cm layer of activated charcoal (E. Merck India Ltd.), 1 x 10 cm layer of silica gel (Glaxo India Ltd.) and approximately 1 x 5 cm bed of anhydrous Na_2SO_4on the top. The concentrated extract was then applied to the pre-washed chromatography column with 40 mL of hexane to remove other contaminants (Picer et al. 1975). The fraction containing organochlorine pesticides were collected, concentrated and transferred to 2 mL volumetric flask and made to volume with hexane to 2 mL (in hexane). Analysis was carried out by using a Varian Aerograph series 2400 equipped with a 3H electron capture detector. A glass column (1.5 m x 2 mm i.d.), packed with 1.5% OV-17 + 1.95% QF-1 on 100-120 mess chromosorb WHP was used. Operation temperatures were 195,200 and 220°C for column,injector and detector respectively. Purified nitrogen gas passing through silica gel and molecular seives was used as carrier gas at a 2 x 10^{-9} A. Data for gas chromatographic analyses were further confirmed by TLC. Procedural blanks, consisting of all reagents and glass-ware used during the analyses, were periodically determined to check the cross contamination. Since no compound that interferred with organochlorine pesticides was detected, the sample values were not corrected for procedural blanks. Recovery studies with fortified sample have inducated that overall recovery

values exceeded 95% except for B-HCH 86%. Results were not adjusted for percent recovery. Identification and quantification were accomplished using a known amount of external standards. The extraction, cleanup and analyses for edible oil samples were essentially the same as desired for oil seeds except high speed homogenization. The saponification values and the percent free fatty acids were estimated according to the method of IUPAC (1979) and AOAC (1984) respectively.

RESULTS AND DISCUSSION

Average concentrations of organochlorine insecticides in different edible oils and oil seeds are summarized in Table 1 and 1a. Presence of alpha, beta and gamma isomers of HCH were found in all samples subjected to GLC analyses. Seasame oil is one of the main components of hydrogenated vegetable oils. Analysis of this oil showed highest level of HCH (Total) followed by groundnut , mustard and other samples of hydrogenated vegetable oils. The concentration of HCH was found to be in the range of 20-4300 ppb. OP'-DDT, P,P'-DDT and their metabolites such as P,P'-DDE and P,P'-DDD were detected in most of the samples. Concentration of DDT (Total) ranged from 36-41620 ppb which suggested its persistence in food chain. Apparently, the transported DDT underwent a metabolic conversion and dehydrochlorination (Matsumura 1973). Presence of DDT and its metabolite (P,P'-DDD) encountered in the oil seed and oil samples in the present study might be due to such metablic processes. Highest content of aldrin was found to be in groundnut oil followed by mustard and hydrogenated vegetable oils. The concentration varied from 11-1130 ppb. Endrin is one of the most toxic organochlorine insecticides (Johnson and Finley, 1980). The levels in sesame and mustard oils were found to be 1960 and 72 ppb respectively. Residues of endusulfan in samples of 4 to 832 ppb. Table 2 presents residues of HCH and DDT in samples of groundnut oil. The values indicated for HCH and DDT are in confirmity with those of earlier observations (Lakshminarayana, 1980, Battu et al. 1980 and Srivastava et al. 1983). However the variation in the level of residues reported by earlier workers and the present study appears to be due to the amount of pesticides used as well as the agro climatic conditions. The present study, has analysed and reported for the first time many other organochlorine pesticides, besides HCH and DDT in edible oils. It has however remained unanswered in what manner the low

Table 1. Residue of pesticides (ppb) in edible oil samples from lcoal markets in Lucknow, India

Pesticides	Groundnut oil	Sesame oil	Mustard Oil	Coconut oil	Vegetable oil
Alpha-HCH	1367 ± 0.25	2100 ± 0.01	860 ± 0.06	18 ± 0.59	30 ± 0.05
Beta-HCH	294 ± 0.25	1200 ± 0.55	260 ± 0.59	2 ± 0.80	90 ± 0.25
Gamma-HCH	413 ± 0.06	1000 ± 0.04	940 ± 0.13	0.8 ± 0.03	10 ± 0.03
Total-HCH	2104 ± 0.15	4300 ± 0.23	2060 ± 0.26	20.8 ± 0.47	130 ± 0.11
pp-DDT	969 ± 0.57	24820 ± 0.29	2270 ± 0.20	-	-
op-DDT	949 ± 0.06	5930 ± 0.20	910 ± 0.70	-	-
pp'-DDT	206 ± 0.58	6000 ± 0.25	1350 ± 0.52	-	4054 ± 0.32
pp'-DDE	1603 ± 0.56	4870 ± 0.03	230 ± 0.58	3.6 ± 0.06	2852 ± 0.52
Total-DDT	3727 ± 0.45	41620 ± 0.19	4760 ± 0.50	3.60 ± 0.01	6906 ± 0.21
Aldrin	1130 ± 0.10	-	75 ± 0.05	-	36 ± 0.08
Endrin	-	1690 ± 0.000	72 ± 0.58	-	6 ± 0.00
Endosulfan	-	-	-	-	4 ± 0.63

Values indicate mean ± SE of 3 estimations.

levels of pesticides residues found in oils have interfered with the health status. This needs more study to link cause effect relationship.

Edible oils and oil seeds have been implicated as a

Table 1a. Residue of pesticides (ppb) in edible seeds from local markets in Lucknow, India

Pesticides	Groundnut oil	Sesame oil	Mustard seed
Alpha-HCH	3.32 ± 0.34	76 ± 0.58	45 ± 0.15
Beta-HCH	211 ± 0.58	7 ± 0.00	16 ± 0.06
Gamma-HCH	7 ± 0.00	9 ± 0.05	30 ± 0.52
Total-HCH	221.32± 0.30	92 ± 0.21	91 ± 0.24
pp'-DDT	-	2050 ± 0.45	_
op'-DDT	-	390 ± 0.15	_
pp'-DDD	50 ± 0.09	100 ± 0.06	750 ± 0.04
pp'-DDE	80 ± 0.67	90 ± 0.06	3 ± 0.00
Total-DDT	130 ± 0.19	2630 ± 0.18	753 ± 0.01
Aldrin	-	-	11 ± 0.01
Endrin	-	-	22 ± 0.83
Endosulfan	8 ± 0.00	22 ± 0.03	832 ± 0.12

Values indicate mean ± SE of three estimations.

source of contamination of human fat (Thakare et al. 1969). It is of interest to note that the maximum occurrence of organochlorine pesticides is always associated with the high lipid content (Richard & Dulley 1983). The saponification value (SV) and percent free fatty acid (%FFA) of different samples of edible oils are shown in Table 2. It was found from these values that sesame oil had the lowest SV and higher content of FFA (percent). It was observed that sesame oil contained more of HCH and DDT in comparasion to other oils and oil seeds (Table 1). A correlation was found between these parameters and the level of HCH and DDT in edible oils.

Organochlorine insecticides known to undergo degradation of elevated temperatures. It is of significance to note rice bran oil when subjected to high temperature was found to convert PCB into PCDF- a

Table 2. Status of saponification values (SV), free fatty acid (FFA%) and residues of HCH and DDT (ppb) in oils and oilseeds in India

Oil seeds/ oil	SV	FFA%	HCH	DDT	References
Groundnut oil	185.13	4.6	Traces	Traces	Lakshminarayana (1980)
			141	-	Battu et al (1980)
			6421	2960	Srivastava et al (1983)
Hydrogenated vegetable oil	185.84	1.92	2104	3728	This report
			130	6906	This report
Mustard oil				22100	Thakare et al (1969)
	201.90	2.71	2060	2490	This report
Sesame oil				10000	Thakare et al (1969)
	180.67	4.05	4300	41620	This report
Coconut oil				9300	Thakare et al (1969)
	257.50	2.05	28	3.60	This report
Groundnut seed				3200	Thakare et al (1969)
			250	130	This report
Mustard seed				1100	Thakare et al (1969)
			91	753	This report
Sesame seed			92	2630	This report

highly toxic substance. Information on behaviour of pesticides in edible oil at light temperature is lacking (Duggan and Duggan 1983). However other factors may also be responsible for the accumulation of organochlorine insecticides and their toxic metabolites in the fat of humans. As the results reported herein are based on a limited number of samples of edible oils

under normal conditions of uses. More studies are required to identify the level of pesticides in oil samples. The paucity of essential data needs a continuous pesticide monitoring programme in different agroclimatic zones of the country.

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