Chick Edema Factor: Removal from Soybean Oil[1]

T.L. MOUNTS, H.J. DUTTON, C.D. EVANS, and J.C. COWAN, Northern Regional Research Laboratory, ARS, USDA, Peoria, Illinois 61604

ABSTRACT

Procedures to remove 2,3,7,8-tetrachlorodibenzodioxin, a potent chick edema factor, have been evaluated in laboratory simulations of commercial deodorization, hydrogenation, and bleaching. Soybean oil samples with 1-5 ppm concentrations of added 2,3,7,8-tetrachlorodibenzodioxin-^{14}C were assayed by liquid scintillation counting before and after processing treatments. Standard conditions of deodorizing were ineffective for removal of 2,3,7,8-tetrachlorodibenzodioxin; extreme conditions (300 C, 10 hr) reduced the concentration appreciably. Although hydrogenating the oil before deodorization improved 2,3,7,8-tetrachlorodibenzodioxin removal under standard conditions, the level of residue was still greater than acceptable. Treating the oil with activated bleaching clay according to the American Oil Chemists' Society standard method was totally ineffective for 2,3,7,8-tetrachlorodibenzodioxin removal. Substituting either of two different activated carbons in the same procedure removed this contaminant from soybean oil.

INTRODUCTION

Chlorinated dibenzo-*p*-dioxins have been identified as the toxic substance in chick edema factor, a disease associated with contaminated fats or oils going into feed (1). 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) is the most toxic of the chlorodibenzo-*p*-dioxins (2), being acnegenic, highly embryotoxic, as well as positive for chick edema factor, that is, producing hydropericardium. Toxic effects in monkeys (3,4) suggest a potential hazard in man. Kimmig and Schulz (5) found that TCDD was formed during production of 2,4,5-trichlorophenol (TCP) by high temperature alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene. TCP is the precursor to 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), a commercial herbicide. TCDD, isolated after thermal decomposition of sodium 2,4,5-trichlorophenate, was fed to rabbits as an oral dose of either 1 or 10 μg/kg (6). The higher level dose killed them all; rabbits administered the lower dosage had serious liver damage and chloracne.

It has been reported that oleic acid, glyceryl monooleates (7), and technical grade chlorophenols (8) contain chick edema factor. Because commercial chlorophenols are widely used as contact herbicides, industrial water additives, termite control agents, defoliants, and as bactericidal and fungicidal agents, opportunities are numerous for fats and fatty acids to become contaminated. Therefore, we conducted laboratory simulations of commercial processing procedures designed to evaluate the efficacy of removing TCDD from soybean oil. Because commercial procedures of alkali refining are ineffective in eliminating chlorinated pesticides from vegetable oils (9), they were not investigated.

MATERIALS AND METHODS

Chlorinated Compounds

The structures of the chlorinated compounds used in these experiments are diagrammed in Scheme I. These compounds, uniformly labeled (UL) with ^{14}C, were obtained through P.C. Kearney, ARS, USDA, from Dow Chemical Co., Midlands, MI (10); 2,3,7,8-tetrachlorodibenzo-*p*-dioxin-^{14}C-UL (TCDD), sp act 2.8 μc/mg; 2,7-dichlorodibenzo-*p*-dioxin-^{14}C-UL (DCDD), sp act 3.6 μc/mg; and 2,4,-dichlorophenol-^{14}C-UL (DCP), sp act 5.9 μc/mg. Each compound was dissolved in benzene (25 ml).

Soybean Oil

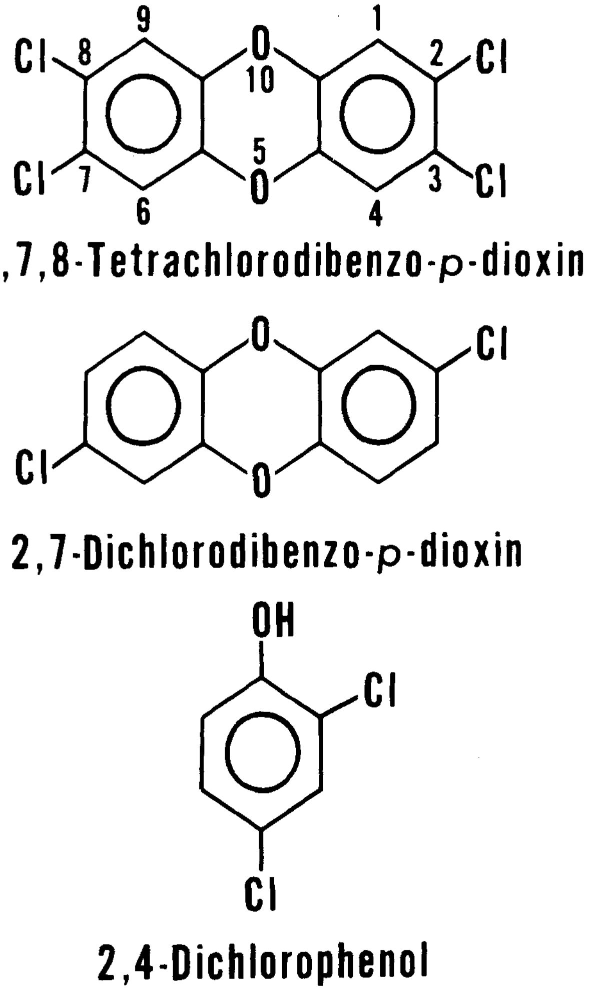
A refined, bleached, and deodorized soybean oil was contaminated by adding a ^{14}C-labeled chlorinated compound in benzene solution to achieve a specific concentration. Each sample was thoroughly mixed before the solvent was evaporated.

Deodorization

High vacuum steam deodorization was simulated in the all glass equipment described previously (11). Commercial deodorization of soybean oil was considered to be performed at temperatures of 180-250 C for 0.5-3 hr and at pressures of 4-30 mm (Hg) with a steam flow rate of 5-10% per hr.

Hydrogenation

Soybean oil was hydrogenated to an iodine value (IV) of



SCHEME 1. Structure of chlorinated compounds.

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[1] Presented at the AOCS Meeting, Dallas, April, 1975.

TABLE I

Removal of Chlorodibenzo-*p*-dioxins-^{14}C-UL[a] by Deodorization

Experiment[a]	Conditions	Steam flow rate (%/hr)	Concentration[b] (ppm) Initial	Final
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin-^{14}C-UL				
1	250 C for 1.5 hr at 4-6 mm	5-10	3.3	1.8
2	250 C for 3 hr at 4-6 mm	5-10	3.3	0.9
3[c]	250 C for 10 hr at 4-6 mm	5-10	3.3	0.025
4[c]	300 C for 1.5 hr at 4-6 mm	5-10	0.9	0.040
5[c]	250 C for 1.5 hr	37	1.8	0.17
6[d]	250 C for 3 hr at 4-6 mm	5-10	2.3	0.19
2,7-Dichlorodibenzo-*p*-dioxin-^{14}C-UL				
1	210 C for 2 hr at 30 mm	5-10	7	0.24
2	240 C for 1 hr at 4 mm	5-10	36	0.11
3	260 C for 1.5 hr at 5 mm	5-10	22	0.12

[a] UL = Uniformly labeled.

[b] Average of duplicate samples.

[c] Probably not practical commercial techniques.

[d] After hydrogenation.

TABLE II

Removal of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin-^{14}C-UL[a] by Bleaching

Experiment	Conditions	Concentration[b] (ppm) Initial	Final
1	110 C, 10 min, 2.4% activated bleaching earth	3.68	3.68
2	110 C, 30 min, 7.7% activated bleaching earth	3.68	3.17
3	110 C, 10 min, 0.64% Norit SS	3.68	0.033
4	110 C, 30 min, 0.52% Norit SS	3.68	0.027
5	110 C, 10 min, 0.57% Norit Ultra C	3.68	0.023
6	110 C, 30 min, 0.9% Norit Ultra C	3.68	0.023
7[c]	110 C, 30 min, 0.9% Norit SS	0.027	0.027

[a] Uniformly labeled.

[b] Average of duplicate samples.

[c] Oil from Expt 4 rebleached.

ca. 100-120 in an all glass manometric hydrogenator (12) simulating batch hydrogenation conditions. Catalyst was 0.1% G-15 nickel (Girdler Catalyst Co., Louisville, KY) at atmospheric pressure and the temperature was 160-165 C.

Bleaching

As described previously (11), commercial bleaching procedures were simulated by stirring each contaminated oil with several bleaching agents at 110 C for 10 and 30 min. Superfiltrol (Johns Mansville, Denver, CO), as used in the AOCS standard method (13), Norit SS and Norit Ultra C (American Norit Co. Inc., Jacksonville, FL), activated carbons, were used as bleaching agents.

Radioassay

Duplicate portions (0.20-1.00 g) of each contaminated oil sample were taken before and after each treatment; these were dissolved in 15 ml of scintillation solvent (7.0 g of 2,5-diphenyloxazole per liter of toluene); and the activity was determined in a Beckman LS-250, three channel liquid scintillation counter equipped with external standardization. The total activity (TA) of each oil sample and the sp act of the added contaminant were used to calculate the concentration:

$$\frac{\text{TA}}{\text{sp act x wt portion}} = \text{concentration.}$$

RESULTS AND DISCUSSION

Laboratory simulations of commercial processing procedures permit wide variation in the conditions used. Soybean oil, contaminated with TCDD-^{14}C to a level of 3.3 ppm, was subjected to deodorization at standard conditions (Table I, Expts 1 and 2). Deodorization for 1.5 hr reduced the concentration of contaminant by $<$ half. Extending deodorization to 3 hr, a practical commercial modification, greatly reduced the concentration; however, the residue was determined to be 0.9 ppm. Extreme conditions of deodorization, having little practical application, were evaluated in Expts 3, 4, and 5 (Table I). Deodorization for 10 hr (Expt 3) was effective in removing TCDD. The residue in the oil after treatment was 0.025 ppm. The concentration of TCDD was similarly reduced by deodorization at 300 C while holding the other variables stable (Expt 4). Increasing steam flow (37% per hr) did not enhance the efficiency of removal (Expt 5). The respective oils recovered from Expts 2 and 1 were used in Expts 4 and 5. These experiments show that while extreme conditions of deodorizations effectively remove TCDD from soybean oil, commercial deodorization techniques are ineffective.

It might be reasonable to expect that the contaminant would be altered during hydrogenation of the oil and thereby be more easily removed. After the contaminated oil sample was hydrogenated to 100-120 IV and filtered, the concentration of TCDD was reduced from 3.3 ppm to 2.3 ppm. This hydrogenated oil was deodorized (Expt 6) under the same conditions used for a nonhydrogenated oil (Expt 2). Evidently, hydrogenation does enhance the effectiveness of deodorization for removal; however, the level achieved is still high.

The efficiency of deodorization to remove a less chlorinated dibenzo-*p*-dioxin was evaluated by treating a soybean oil contaminated with DCDD-^{14}C-UL. Procedural conditions were varied; all variations were within the range of standard commercial techniques as defined earlier. Although initial contamination of the oil sample in each experiment differed, the final concentration was relatively the same. Apparently, reducing the number of chlorine atoms in the parent compound does enhance the efficiency of standard deodorization techniques for removal of contamination.

Methods of bleaching soybean oil were also evaluated (Table II). Soybean oil was contaminated with TCDD-^{14}C at a concentration of 3.68 ppm. An activated bleaching earth (13) had little effect in removing TCDD (Table II, Expts 1 and 2). In Expt 2 the efficiency of removal was not enhanced either by a threefold increase in the amount of bleaching earth or by tripling the bleaching time. In Expts 3-6, the TCDD was almost totally removed by bleaching with an activated carbon. Evidently the type of bleaching agent is the determining factor for increased efficiency of removal because neither length of bleaching time nor amount of bleaching agent altered the results. This finding agrees with our previous work with benzo-α-pyrene (12), a nonchlorinated high mol wt hydrocarbon, that activated carbon is necessary to ensure removal of the contaminant. As a final experiment, soybean oil contaminated with DCP-^{14}C (1.91 ppm), a compound characterized as being frequently contaminated with TCDD, was bleached atmospherically with 0.1% Norit Ultra C for 60 min at 130 C. DCP is removed from the oil by this procedure as effectively as was TCDD; the final concentration of DCP was 0.054 ppm.

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