at the retention time of OZT. This was confirmed by spiking the extract with a known quantity of OZT. A peak appeared after 8.5 min in the milks from six western dairies, but this peak was not detected in milk from three dairies in Ontario.

DISCUSSION

The level of OZT in milk in Finland was reported to be as high as 35–100 µg/L of milk (Arstila et al., 1969). Formerly levels of OZT less than 100 µg/L were considered to be insignificant because this amount does not inhibit radioiodine uptake (Virtanen et al., 1963). Rats dosed orally with 500 ng of OZT daily for 2 weeks showed significant thyroid enlargement but radioiodine uptake was not affected (Krusius and Peltola, 1966). The lowest single dose required to inhibit radioiodine uptake was found to be 500 µg which is 1000 times greater than the oral daily dose required to produce enlargement of the rat thyroid. A single oral dose of 25 mg of OZT inhibited radioiodine uptake in adult human (70 kg) (Langer et al., 1971). Extrapolation from the results obtained for rats indicates that thyroid enlargement is possible at an OZT level of 2 µg/L of milk for an infant of 6 kg ingesting 1 L of milk per day.

With the extraction procedure described and the use of LC, relatively small volumes (50 mL) of milk can be analyzed to detect levels of OZT as low as 1–2 µg/L.

Analysis of pasteurized milk samples from six western and three eastern dairies indicated that the winter milk supply from these dairies did not contain OZT in amounts greater than 2 µg/L. An unknown compound with a retention time, close, but not identical with that of OZT, was detected in milk from six western dairies.

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Extraction of Free and Bound Carboxylic Acid Residues from Field Soils Treated with the Herbicides Benzoylprop-ethyl, Diclofop-methyl, and Flamprop-methyl
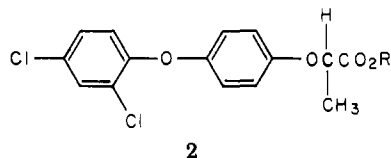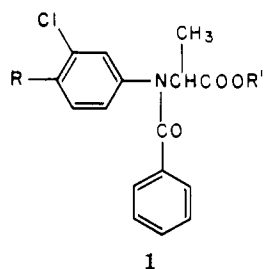
Allan E. Smith

The breakdown of the herbicidal esters benzoylprop-ethyl, diclofop-methyl, and flamprop-methyl was studied in small field plots at three locations in Saskatchewan after two separate growing seasons. Following extraction of soil samples with aqueous acidic acetonitrile, the parent esters and acid hydrolysis products were determined gas chromatographically. Residues of benzoylprop-ethyl and flamprop-methyl, together with their corresponding acids, were recovered from treated soils at all sites both years, whereas no significant amounts of diclofop-methyl (or acid) were observed in any sampled soils. Following extraction with the acidic acetonitrile solvent, the soil residua were reextracted with cold aqueous sodium hydroxide or hot aqueous triethanolamine solutions to release any benzoylprop, diclofop, or flamprop acids held on the soil in a bound form. From these alkaline digestion studies and experiments conducted to compare the extractions of the three herbicidal acids from fortified soils using cold sodium hydroxide and hot triethanolamine as extractants, it was concluded that any such bound residues could only be present in negligible quantities.

The herbicidal esters benzoylprop-ethyl [1, R = Cl, R′ = C_2H_5; ethyl (±)-2-[*N*-(3,4-dichlorophenyl)benzamido]-propionate], diclofop-methyl [2, R = CH_3; methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate], and flamprop-methyl [1, R = F, R′ = CH_3; methyl (±)-2-[*N*-(3-chloro-4-fluorophenyl)benzamido]propionate] are used at

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rates of approximately 1 kg/ha for the control of wild oats (*Avena* sp.) and other annual grasses in a variety of crops.

Although these herbicides are applied as postemergence treatments, some of the spray can come into contact with the soil where they undergo hydrolysis to their respective carboxylic acids (Beynon et al., 1974; Roberts, 1977; Smith, 1977). Initially these acids can be recovered almost quantitatively from treated soils using acidic polar solvent mixtures (Wright and Mathews, 1976; Smith, 1976, 1977). Using ^{14}C-labeled herbicides it has been shown that with

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time both benzoylprop acid (Beynon et al., 1974) and diclofop acid (Smith, 1977) become bound to the soil and consequently resistent to extraction using polar acidic solvent mixtures. These bound acids could, however, be released from the soils by treatments with hot alkali (Beynon et al., 1974; Smith, 1977).

Aqueous sodium hydroxide has been recommended by the Environmental Protection Agency (cf. Kearney, 1976) for the extraction of bound pesticide residues from soils, and the procedure involves the treatment of soils, following normal solvent extraction, with the base at room temperature.

The work to be described was undertaken to determine the extent to which the carboxylic acids derived from benzoylprop-ethyl (1, R = Cl, R′ = C_2H_5), flamprop-methyl (whose structure 1, R = F, R′ = CH_3 is very similar to that of benzoylprop-ethyl), and diclofop-methyl (2, R = CH_3) are bound to field soils at the end of the growing season following application. Since alkaline treatments appear to be necessary for removal of the bound acid residues from soils, preliminary studies were conducted to compare the recoveries of benzoylprop, flamprop, and diclofop acids from three fortified soil types using aqueous sodium hydroxide at room temperature and boiling aqueous triethanolamine as extractants. The recoveries of the three carboxylic acids from centrifuged alkaline extracts derived from the three soil types was also examined to check for possible adsorption of the chemicals to precipitated organic matter during work up. Finally, soils from small field plots at three locations, individually treated during May of 1976 and 1977 with benzoylprop-ethyl, diclofop-methyl, and flamprop-methyl were sampled at the end of each growing season (in October) and extracted with polar solvents to recover for analysis any unbound ester and carboxylic acid residues. The soil residua were then reextracted with cold sodium hydroxide and boiling aqueous triethanolamine to determine any bound carboxylic acid residues thus released as the respective free acids.

MATERIALS AND METHODS

Soils. The composition and physical characteristics of the soils referred to in this study are summarized in Table I.

Chemicals. Diclofop-methyl and diclofop acid (purity greater than 99%) were obtained from Hoechst Aktiengesellschaft, Frankfurt, Germany, while benzoylprop-ethyl, benzoylprop acid, flamprop-methyl, and flamprop acid, with purities in excess of 99%, were provided by Shell Research Ltd., Sittingbourne, England. The pure carboxylic acids were used in the laboratory recovery studies for which individual solutions were prepared containing 1.0 mg of the respective acid per milliliter of ethanol.

Table I. Composition and Physical Characteristics of Soils

soil type	composition, %					field capacity moisture, %
	clay	silt	sand	organic content	pH	
Jameson, sandy loam (SL)	6	9	85	3	7.5	11
Melfort, silty clay (SiC)	30	38	32	12	5.2	36
Regina, heavy clay (HvC)	69	26	5	4	7.7	40

For the field persistence studies, formulated samples of the herbicidal esters were utilized. Diclofop-methyl was obtained from Hoeschst Aktiengesellschaft, Frankfurt, Germany, as an emulsifiable concentrate (0.36 kg/L). Emulsifiable concentrates of both benzoylprop-ethyl (0.20 kg/L) and flamprop-methyl (0.15 kg/L) were supplied by Shell Agrochemicals Development, Toronto, Canada. Individual ethanolic solutions of these technical materials were prepared containing 3.0 mg/mL of benzoylprop-ethyl or diclofop-methyl and 2.0 mg/mL of flamprop-methyl.

Field Studies. Unincorporated treatments of the ethanolic ester solutions (2.0 mL) were made to separate field plots (20 × 20 cm) at each of the three locations using the procedure described by Smith (1971, 1975). These rates, equivalent to 1.5 kg/ha for benzoylprop-ethyl and dichlofop-methyl and 1.0 kg/ha for flamprop-methyl, are those commonly used for weed control in western Canada. Three replicate plots for each chemical were treated during the second week of May 1976 and 1977, respectively. All plots remained fallow and were hand-weeded as necessary. Treatments were sampled by removing the soil from the 0–5 and 5–10 cm levels of each plot as previously reported (Smith, 1971, 1975). After air-drying and grinding, the individual soil samples were weighed and mixed in a laboratory mixer for 15 min.

Extraction of Unbound Residues. Soil subsamples (20 g) were extracted with 50 mL of 10% aqueous acetonitrile and the herbicidal esters recovered determined gas chromatographically. Further subsamples of the soils (20 g) were shaken with 50 mL of 30% aqueous acetonitrile containing 2% of glacial acetic acid, and the extracts were analyzed for unbound carboxylic acid residues. Full details for these extractions, analyses, and recoveries have been reported elsewhere (Smith, 1976).

Soil residua, following treatment with the acidic aqueous acetonitrile to remove unbound ester and carboxylic acid residues, were collected and washed twice with methanol, the washings being discarded. The soils were then dried to constant weight at 50 °C.

Sodium Hydroxide Extraction. Samples (20 g) of the soils, following organic solvent extraction, methanol washing, and drying were shaken with 50 mL of 0.5 N aqueous sodium hydroxide on a wrist-action shaker for 1 h. Following centrifugation at 3000 rpm for 5 min, 25 mL of the dark-brown extracts (equivalent to 10 g of soil), in 50-mL capacity glass centrifuge tubes, were acidified with 10 mL of concentrated hydrochloric acid. The tubes were cooled in iced water for exactly 5 min and recentrifuged to separate the humic acid precipitates. The clear yellow supernatants, containing the soluble fulvic acids, were decanted into 250-mL separatory funnels, diluted with 100 mL of water, and shaken with 2 × 50 mL portions of diethyl ether. Pooled ether extracts were evaporated to dryness at 30 °C using a rotary evaporator. Traces of water were removed from flasks by azeotropic distillation under reduced pressure following the addition of equal volumes

of methanol and benzene. The residues were quantitatively transferred, using ether, to 50-mL glass tubes and methylated using 2 mL of an ether solution containing diazomethane (Rivers et al., 1970). Excess reagent and ether were evaporated by means of a hot water bath at 50 °C. Complete removal of the ether was avoided to preclude ester losses by volatility. The solution volumes were adjusted to 50 mL with hexane and suitable aliquots (5 µL) analyzed gas chromatographically for carboxylic esters.

Hot 80% Aqueous Triethanolamine Extraction. Samples (20 g) of the soils following organic solvent extraction etc. were heated under reflux (using an oil bath at 115 °C) with 50 mL of 80% aqueous triethanolamine. After cooling, the contents of the flasks were centrifuged at 3000 rpm for 5 min when 25 mL of the dark extracts were acidified, cooled, recentrifuged, ether extracted, and methylated in precisely the same manner as described for the sodium hydroxide extraction above.

Recoveries from Fortified Soils. Twenty-gram samples of air-dried sandy loam, silty clay, and heavy clay were weighed into 125-mL capacity glass-stoppered flasks and treated with 50 µL (50 µg) of the pure benzoylprop, diclofop, or flamprop acid solution under test. This rate of 2.5 ppm is approximately equivalent to a field rate of 1 kg/ha assuming soil incorporation to a depth of 5 cm. After thorough mixing, the treated soils were left to equilibrate at laboratory temperature for 48 h.

Duplicate samples were extracted using 0.5 N aqueous sodium hydroxide and boiling 80% aqueous triethanolamine exactly as described above and the amounts of the various acids recovered determined.

Recoveries from Fortified Alkaline Soil Extracts. To duplicate 25-mL portions of centrifuged soil extracts [obtained by shaking untreated soils (20 g) with either 0.5 N sodium hydroxide (50 mL) for 1 h or boiling 80% aqueous triethanolamine (50 mL) for 5 h] were added 25 µg (25 µL) of benzoylprop, diclofop, or flamprop acids. The extracts were thoroughly mixed for 15 s to disperse the herbicidal acids and immediately acidified with 10 mL of concentrated hydrochloric acid to precipitate the humic acids. Following cooling for 5 min, centrifugation, and ether extraction etc., the herbicidal acids were determined gas chromatographically.

Recovery blanks were carried out by adding 50 µg (50 µL) of the respective carboxylic acid to 50 mL of 0.5 N sodium hydroxide or 50 mL of 80% aqueous triethanolamine in the absence of soil. The solutions were then either shaken for 1 h or boiled for 5 h before extraction and analysis.

Gas Chromatography. The Hewlett-Packard 5713 A gas chromatograph used in these studies was equipped with on-column injection facilities and a radioactive nickel detector operated at 300 °C. The glass column (1.5 m × 4 mm i.d.) was packed with 10% OV-1 on 80–100 mesh Chromosorb G, HP. Argon containing 5% of methane at a flow rate of 40 mL/min was the carrier gas. With a column temperature of 240 °C, the retention times for benzoylprop-ethyl, benzoylprop-methyl, diclofop-methyl, and flamprop-methyl were 12.0, 10.5, 10.5, and 6.3 min, respectively. Esters present in the samples were calculated by comparing sample peak heights with those of appropriate standards (in hexane). Analysis of untreated soils confirmed the absence of interfering substances.

RESULTS AND DISCUSSION

The recoveries of the carboxylic acids from the alkaline blanks and fortified soils are summarized in Table II. There was a variation of less than ±5% between each replicate extraction and analysis. In the absence of soil,

Table II. Recoveries of Benzoylprop, Diclofop, and Flamprop Acids from Fortified Soils (2.5 µg/g) Using 0.5 N Sodium Hydroxide and Boiling 80% Aqueous Triethanolamine as Extractants

| | % of applied herbicidal acid recovered[a,b] | | | | | |
| | benzoylprop acid | | diclofop acid | | flamprop acid | |
soil type	Na-OH	tri-etha-nol-amine	Na-OH	tri-etha-nol-amine	Na-OH	tri-etha-nol-amine
SL	39	43	5	65	56	35
HvC	93	92	53	90	93	40
SiC	28	25	5	25	43	12
blank/ no soil	98	100	95	94	95	93

[a] Average from duplicate experiments. [b] 50 µg of acid added to 20 g of soil and extracted with 50 mL of base.

over 90% of the three carboxylic acids could be recovered, thus confirming that no degradative or other losses had occurred as a result of the respective treatments. In general, recoveries of the herbicidal acids from the soils using the two alkaline solvents was poor (Table II) and in direct contrast with acidic polar solvent mixtures which are known to extract these chemicals almost quantitatively from a variety of soil types (Wright and Mathews, 1976; Smith, 1977). Cold aqueous sodium hydroxide was superior to hot triethanolamine for recovering flamprop acid from all soils, while for diclofop acid the reverse was true (Table II). Both treatments appeared to be equally effective for the extraction of benzoylprop acid residues from the fortified soils. Regardless of extraction procedure used, recoveries of all three acids were greatest from the heavy clay and least from the silty clay.

It is generally accepted that treatment of soil with alkaline solutions effects extraction of organic matter, the humic acid fraction of which is precipitated by acidification of the alkaline extract, while fulvic acids, being acid soluble, remain in the aqueous acidic solution (cf. Kearney, 1976). However, it has been pointed out (cf. Schnitzer and Khan, 1972; Stevenson, 1976) that soil organic matter can form complexes with clay minerals that are soluble in alkaline solutions. Thus, if these complexes are precipitated on acidification, the humic fraction could contain additionally some of these clay complexes.

No attempts were made to quantitatively measure the humic content of the soils studied although it was noted that the Regina heavy clay contained the least amounts of humic substances since acidification of alkaline extracts produced only a faint precipitate. The Melfort silty clay yielded the greatest humic precipitate. Hot triethanolamine soil treatments tended to give slightly greater amounts of humic substances on acidification than those derived from sodium hydroxide.

The extent of herbicide adsorption to adsorbents can be greatly affected by pH (cf. reviews of Bailey and White, 1964; Hamaker and Thompson, 1972; Adams, 1973). Thus, in solutions of low pH weakly acidic pesticides in the free acid state would be adsorbed to a greater extent than the neutral anionic form (Hamaker and Thompson, 1972). Experiments by Grover (1968) with picloram and Ward and Getzen (1970) with 2,4-D have confirmed this increased adsorption with lowering of pH.

Hence, the low recoveries encountered for the alkaline extractions of benzoylprop, diclofop, and flamprop acids (Table II) from fortified soils could be due in part to the adsorption of extracted herbicidal acids to precipitated humic materials during work up. The recoveries of

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Table III. Recoveries of Benzoylprop, Diclofop, and Flamprop Acids from Centrifuged Alkaline Soil Extracts

| | % of applied carboxylic acid recovered[a,b] | | | | | |
| | benzoylprop acid | | diclofop acid | | flamprop acid | |
soil extract	Na-OH	tri-etha-nol-amine	Na-OH	tri-etha-nol-amine	Na-OH	tri-etha-nol-amine
SL	75	54	39	29	80	57
HvC	88	78	72	70	97	78
SiC	21	35	5	12	35	41

[a] Average from duplicate experiments. [b] 25 μg of acid added to 25 mL of centrifuged extract obtained by treating 20 g of soil with 50 mL of base.

benzoylprop, diclofop, and flamprop acids from centrifuged alkaline soil extracts (Table III) confirmed this hypothesis since in all cases the herbicidal acid recoveries were greatest from the heavy clay extracts (with the least humic content) and least from the silty clay extracts (with the highest humic content).

For some unexplainable reason the recoveries of diclofop acid from the centrifuged soil extracts derived from triethanolamine were considerably lower (Table III) than the triethanolamine induced recoveries from the fortified soils (Table II). In all other instances amounts of the carboxylic acids recovered from the fortified soils were equal to or less than those recovered from the fortified alkaline extracts (Tables III and II).

Although diclofop acid appeared to be adsorbed to the humic fraction of the silty clay and sandy loam to a greater extent than benzoylprop and flamprop acids (Table III), care must be taken in interpreting these results. Hance (1967) and Hamaker and Thompson (1972) have reported that the time for adsorption equilibrium to be established under slurry conditions can take as long as 24 h. In the present experiments equilibrium adsorption times were not studied and only 5 min were allowed to lapse between acidification and removal of humic precipitates by centrifugation. Thus, the data displayed in Table III probably represent differing stages in the adsorption process with, for example, one chemical almost at adsorption equilibrium while another may be nowhere near equilibrium.

Certain tentative conclusions may be drawn from these fortification studies. Using alkaline extractants, efficient recoveries of benzoylprop, diclofop, and flamprop acids could only be achieved from soils low in humic acids. The nature of the alkaline extractant seemed to be of importance since cold aqueous sodium hydroxide was as good, or better, than hot triethanolamine for recovering residues of benzoylprop and flamprop acids, whereas the reverse was true for diclofop acid. Clearly more work is necessary to show whether diclofop acid is exceptional in requiring hot, rather than cold, alkaline treatments for adequate recovery and to determine whether the heating of the soil with aqueous triethanolamine alters the nature of the soil components to render the diclofop acid more accessible to extraction. A major concern for attention is that a portion of the carboxylic acid residues extraced by alkaline procedures can be readsorbed to precipitated humic substances during work up. This is of great importance since if this is a general phenomenon and can occur with other pesticide products, residues may erroneously be assumed to be bound to soils and therefore resistant to alkaline extraction. At least some of the reported soil-bound residues derived from benzoylprop-ethyl (Beynon et al., 1974) and diclofop-methyl (Smith, 1977) may be

Table IV. Residues Recovered from the Top 5 cm of Field Plots at Three Locations in October 1976 and 1977 following Applications of Herbicidal Esters in May 1976 and 1977

		% of applied ester remaining as[a]																	
		Jameson (SL)						Regina (HvC)						Melfort (SiC)					
		ester[b]		acid[c]		bound acid[d]		ester[b]		acid[c]		bound acid[d]		ester[b]		acid[c]		bound acid[d]	
chemical	rate, kg/ha	1976	1977	1976	1977	1976	1977	1976	1977	1976	1977	1976	1977	1976	1977	1976	1977	1976	1977
benzoylprop-ethyl	1.5	2 ± 1	14 ± 1	4 ± 2	11 ± 3	<5	<5	11 ± 1	9 ± 2	13 ± 1	6 ± 1	<5	<5	19 ± 3	20 ± 1	16 ± 2	13 ± 1	<5	<5
diclofop-methyl	1.5	<2	<2	<5	<5	<5	<5	<2	<2	<5	<5	<5	<5	<2	<2	7 ± 1	<5	<5	<5
flamprop-methyl	1.0	2 ± 1	12 ± 2	5 ± 2	5 ± 3	<5	<5	12 ± 3	14 ± 2	6 ± 1	8 ± 2	<5	<5	22 ± 5	21 ± 1	6 ± 2	16 ± 4	<5	<5

[a] Average from three plots mean and standard deviation, no residues detected in the 5–10 cm soil levels. [b] Extracted using 10% aqueous acetonitrile. [c] Extracted using 30% aqueous acetonitrile containing 2% glacial acetic acid. [d] Soils were first extracted with solvent c and the residua then reextracted by shaking with 0.5 N sodium hydroxide for 1 h or by boiling with 80% aqueous triethanolamine for 5 h.

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attributed to such a source. Clearly, new methodology is needed to better evaluate the problem of bound residues, and new extractants tried which may result in minimizing readsorption problems.

The results of field studies (Table IV) indicated that over each of the two growing seasons diclofop-methyl had undergone almost complete degradation since no significant amounts of ester or unbound acid residues were recovered from any of the treated soils. In contrast, carryover of unbound ester and acid residues derived from benzoylprop-ethyl and flamprop-methyl were observed both years at all three locations (Table IV). Both chemicals were more persistent in the Melfort silty clay with approximately 30–40% of the applications remaining in the ester and acid forms, while in the heavy clay and sandy loam the figures ranged from 15–23 and 6–25%, respectively. No unbound residues were detected at depths greater than 5 cm, indicating that leaching of these chemicals under field conditions should not be a problem.

In every case, following extraction of unbound residues, reextraction of the soil residua with aqueous sodium hydroxide and boiling triethanolamine solution failed to release detectable amounts of benzoylprop, diclofop, or flamprop acids.

In view of the laboratory fortification studies (Tables II and III) and considering that under field conditions the acid residues (bound) could be present in smaller quantities than those used (2.5 ppm) in the above studies, it was necessary to confirm that the absence of bound carboxylic acid residues was not simply due to inadequate analytical techniques. Hence, samples of untreated soils (20 g) were fortified with 3 μg of either benzoylprop or diclofop acids or 2 μg of flamprop acid. These amounts, equivalent to 0.15 and 0.10 ppm, respectively, were those which could be released from treated field plots (2 kg/plot) if it were assumed that bound acid residues accounted for 5% of the original ester applications. These fortified soils were then extracted using cold aqueous sodium hydroxide and hot triethanolamine solutions as described. Although quantitative analysis was impossible because of interferences on the chromatograms resulting from the high attenuation necessary for detection, peaks due to the respective methyl esters were clearly discernible in all cases, though not on the chromatograms derived from the soil blanks or from the treated field plots. This was taken as confirmation that after a growing season the field soils contained negligible carboxylic residues (less than 5% of the original ester treatments) in a bound form. Since the herbicidal esters are normally applied as postemergence treatments and not directly to the field plots as they were in this study, bound residues derived from benzoylprop, diclofop, and flamprop acids should be insignificant following normal field applicatons.

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Essential Oil of *Eucalyptus globulus* in California

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Analysis of the *Eucalyptus globulus* essential oil by using mainly the computerized gas chromatography–mass spectrometry revealed 1,8-cineol, α-, β-, and γ-terpinene, β-pinene, terpinen-4-ol, linalool oxide, α-gurjunene, aromadendrene, alloaromadendrene, globulol (10-hydroxyaromadendrane), and so on. The gas–liquid chromatography comparisons of terpene fractions of the fresh *Eucalyptus* fruits indicated that sesquiterpenes were more significant than monoterpenes. In case of the shoots, monoterpenes such as 1,8-cineol and γ-terpinene were major rather than sesquiterpenes. The plant oil as a renewable source of hydrocarbon-like photosynthetic products was evaluated in connection with the utilization of solar energy.

As a result of decreasing supplies of fossil hydrocarbons it has become necessary to reexamine other sources of raw

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materials for possible conversion into hydrocarbons (Calvin, 1974, 1976). In connection with the utilization of solar energy for renewable resources, we have reported the constituents of photosynthesizing plants such as rubber tree (*Hevea brasiliensis*), some different species of *Euphorbia*, and other latex-bearing plants which grow naturally in tropical and temperate regions (Nishimura et al., 1977; Nielsen et al., 1977). The results have indicated that those plants contain a large amount of lipids such as