plots larger than 0.5 ha. Replications of the plots were impossible as was also repetition of the treatments a second year. Therefore, from the entire seed stock from each treatment plot, quadruplicate seed samples were utilized as replications. Statistical analysis was conducted on a randomized block design for each fatty acid component, and mean differences were separated by the Duncan's multiple range test.

Common names, chemical names, formulations, application rates, and application sequences of herbicides applied to the several plots are shown in Table II.

RESULTS AND DISCUSSION

Eight sequential herbicide programs were utilized for cotton culture. None of these cultural programs resulted in a major change in the cottonseed oil quality of the treated crop. Six of the nine compounds utilized in the sequential programs in this test were reported as single herbicide applications by Wilkinson and Hardcastle (1971). Cottonseed oil quality was not greatly influenced by those six herbicides individually. Wilkinson and Hardcastle (1971) reported soil type, season, and location to have a greater influence on cottonseed oil quality than any of the six individual herbicides.

Because the cotton grown in this test was grown for genetic seed stock increase, the treatments could not be replicated in a normal agronomic test plot pattern. However, the plots were large enough to preclude major sampling errors. Comparison of the data from these analyses and those presented previously (Wilkinson and Hardcastle, 1971) indicated that the variability of cottonseed oil quality from these eight sequential herbicide programs was not greater than was found to be due to location or season. The variability of cottonseed oil quality from cotton grown on the same soil type during the same growing season was greater (Wilkinson and Hardcastle, 1971) than was found within these eight sequential herbicide programs.

Thus it must be concluded that these eight sequential herbicide programs on cotton, including the use of these nine herbicides at registered application rates, do not deleteriously influence the quality of cottonseed oil.

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Optically Pure Pyrethroids Labeled with Deuterium and Tritium in the Methylcyclopentenonyl Ring

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A convenient procedure is described for preparing 100-mg quantities of (+)-pyrethrolone and (+)-allethrolone labeled with ^{3}H in the methyl and methylene groups of the ring and for converting them to the corresponding esters, pyrethrins I and II, and allethrin, optically and stereochemically pure and with specific activities of 317–675 mCi per mmol. Pentadeuteroallethrolone and pentadeuteroallethrin were prepared as model compounds to establish the positions of labeling. The radiolabeled esters were sufficiently stable to be used in metabolism and mode-of-action studies, because there was no evidence of interference from radiation-induced decomposition or of isotopic exchange under biological conditions.

Research on the metabolism and mode of action of the natural pyrethrins has been hampered by lack of convenient procedures for radiosynthesis of adequate quantities of the pure isomers of these compounds with sufficient specific activity. The two most important esters in the natural material, from the flower heads of *Chrysanthemum cinerariaefolium*, are pyrethrin I and pyrethrin II (Figure 1). Of the 16 possible stereoisomers of pyrethrin I (I) and 32 of pyrethrin II (II) (Crombie and Elliott, 1961), the two natural forms probably have the highest insecticidal activity. Therefore, for metabolic and mode of action studies it is important that the products from radiosynthesis consist only of the pure, separated, optical and geometrical forms found in nature.

^{14}C-(+)-*Trans*-chrysanthemic acid (III, ^{14}C at *) was prepared and esterified with (+)-pyrethrolone (IV) and (+)-allethrolone (IV) (Nishizawa and Casida, 1965; Yamamoto and Casida, 1968) but pyrethrins I and II have not previously been available with a radioisotope in the alcohol moiety (Elliott *et al.*, 1970). Although natural and synthetic cyclopentenolones, including (±)-pyrethrolone, have been synthesized (Crombie *et al.*, 1950, 1969; Schechter *et al.*, 1949), no adequate method for optical resolution easily adapted to small quantities has yet been developed; thus only ^{14}C-(±)-allethrolone is available so far (Winteringham *et al.*, 1955; Yamamoto and Casida, 1968). We therefore examined the possibility of introducing tritium into (+)-pyrethrolone (IV) which is readily accessible from natural pyrethrum extract (Elliott, 1964; Maciver, 1968). ^{3}H-Labeling has some advantages over synthesis of compounds with ^{14}C, because products of high specific activity can often be made at reasonably low cost by exchange reactions of protons in the molecule with the tritium in tritiated water, which is available at high specific activity. If the center of optical activity in the molecule is remote from the exchanging positions, reaction conditions

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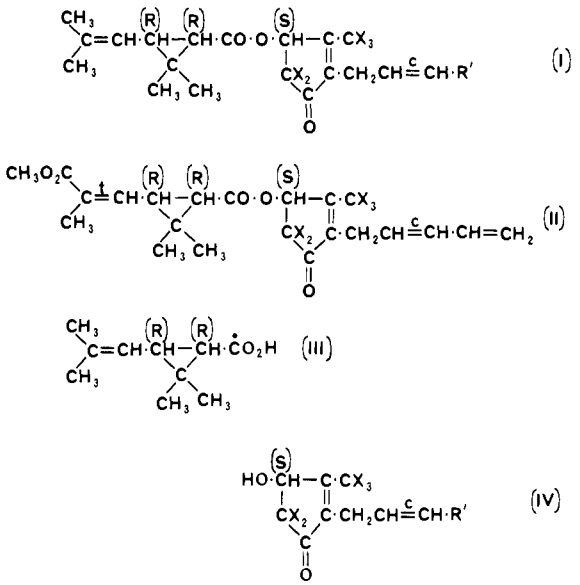

Figure 1. Structures of pyrethrin I (I, R′ = CH=CH₂, X = H); pyrethrin II (II, X = H); allethrin (I, R′ = X = H); chrysanthemic acid (III); pyrethrolone (IV, R′ = CH=CH₂, X = H); and allethrolone (IV, R′ = X = H)

mild enough to avoid racemization may be found. Uncertainty as to the positions at which tritium enters the molecule and its stability there can often be partly or wholly resolved by examining comparable systems with deuterium or deuterium oxide by nuclear magnetic resonance (nmr) spectroscopy.

A simple procedure for radiosynthesis, by which the (+)-cyclopentenolones (IV) were heated with tritium oxide containing potassium carbonate, was developed to prepare (+)-[5-CH_2,3-CH_3-^{3}H]-4-hydroxy-3-methyl-2-alkenyl-cyclopent-2-enones of high specific activity. These alcohols were converted to ^{3}H-pyrethrin I (I, ^{3}H at X) and ^{3}H-allethrin (I, ^{3}H at X) by reaction with (+)-*trans*-chrysanthemic acid chloride, and to ^{3}H-pyrethrin II (II, ^{3}H at X) by reaction with (+)-pyrethric acid chloride.

MATERIALS AND METHODS

Chromatography columns (2 × 20 cm) packed with Florisil (50 g, 100 mesh for chromatography; Floridin Co., Tallahassee, Fla.) were developed with 100 ml each of hexane, various ether–hexane mixtures containing from 10 to 70% ether, and finally with pure ether. Eluted fractions (10 ml) were assayed for tritium content and, by thin-layer chromatography (tlc), for compounds detected under ultraviolet light or with phosphomolybdic acid reagent (Yamamoto *et al.*, 1969). Chromatoplates for tlc (silica gel F_{254}, 0.25 mm gel thickness, Brinkmann Instruments Inc., Westbury, N.Y.) were developed with ether–hexane (2:1) mixture to give R_f values as follows: pyrethrin I, 0.57, pyrethrin II, 0.44, and allethrin, 0.59. Tritium-labeled compounds were detected on the tlc plates by radioautography as follows: the gel was sprayed to produce thick even coverage (confirmed by uv fluorescence) with Liquiflor (25× concentrated scintillation mixture, Nuclear Chicago Corp., Des Plaines, Ill.), and dried; Kodak Blue Brand X-ray film was placed directly on the plates and exposed for 1 to 3 days at −80°C before development. This procedure detects 10,000 dpm of a compound after 3 days' exposure.

Ultraviolet absorption spectra were determined for ethanol solutions with a Beckman DU spectrophotometer. Nmr spectra were determined in deuterochloroform or carbon tetrachloride, using tetramethylsilane as internal standard, or in deuterium oxide with a Varian T60 spectrometer. Mass spectra were recorded on a Perkin-Elmer Hitachi RMU6E spectrometer for samples introduced *via* the all-glass inlet system. Optical rotations were measured with an ETL-NPL Automatic Polarimeter Type 143A (Bendix Ericsson, U.K., Ltd., Nottingham, Great Britain). The Beckman LS-150 liquid scintillation spectrometer was used for quantitative radioactivity measurements.

The pyrethrins are unstable when exposed to light and air and so they were manipulated whenever possible in the dark; solutions containing these compounds were concentrated in oxygen-free nitrogen.

SYNTHESES

Pentadeuteroallethrolone. (IV, R′ = H, X = ^{2}H). (±)-Allethrolone (10 ml; Sumitomo Chemical Co., Osaka, Japan) was purified by heating on steam for 45 min with 1% potassium carbonate (100 ml); sodium chloride was added and the ketol was extracted into ether. The ether solution was washed with saturated sodium chloride, dried (sodium sulfate), and evaporated. Distillation of the residue gave (±)-allethrolone (5.0 g): bp 105.5–107.5°C/0.05 mm, n^{24}D 1.5150. Nmr showed that this product was approximately 95% pure (small impurity at τ 8.63). Purified (±)-allethrolone (2.1 g) was then heated on steam for 1 hr with deuterium oxide (15 ml, 99.5%) containing 1% potassium carbonate. After adding sodium chloride, the deuteroallethrolone that separated was taken up in benzene (3 × 5 ml). The benzene extracts were passed through a short column of anhydrous sodium sulfate, and then the solution was concentrated. The residue was heated again with deuterium oxide containing 1% potassium carbonate (20 ml), processed as before, and distilled to give pentadeuteroallethrolone (1.2 g): bp 89–90°C/0.005 mm, n^{21}D 1.5189, [M^+ 157 ($C_9{}^2H_5H_7O_2$), 139 (M − C^2H_3), 129 (M − CO); (±)-allethrolone showed M^+ 152 ($C_9H_{12}O_2$), 137 (M − CH_3), 124 (M − CO)].

Pentadeuteroallethrin. (I, R′ = H, X = ^{2}H). (±)-Pentadeuteroallethrolone (0.65 g), the chloride of (+)-*trans*-chrysanthemic acid (Elliott and Janes, 1969) (1.0 g), and pyridine (0.43 g) dissolved in benzene (10.9 ml) were kept at 25°C for 19 days (see DISCUSSION), and then the reaction mixture was added to alumina (5 g; Woelm neutral) and eluted with benzene (30 ml). After evaporating the benzene, the product was taken up in ether, washed with saturated sodium chloride solution, dried (sodium sulfate), and distilled after evaporating the solvent to give pentadeuteroallethrin (0.9 g): bp 131–133°C/0.005 mm, n^{20}D 1.5051, [M^+ 307; other peaks at 168 ($C_{10}H_{16}O_2$, chrysanthemic acid), 153 ($C_{10}H_{16}O_2$ − CH_3), 141 (see DISCUSSION), 123 ($C_{10}H_{16}O_2$ − CO_2H) and 112 (see DISCUSSION); (±)-allethronyl (±)-*trans*-chrysanthemate showed M^+ 302; other peaks at 168 ($C_{10}H_{16}O_2$), 153, 136, 123 and 107].

^{3}H-Pyrethrin I. (I, R′ = CH=CH_2, ^{3}H at X). (+)-Pyrethrolone hydrate (0.118 g; 0.6 mmol; Elliott, 1964), anhydrous potassium carbonate (0.018 g) and dimethyl formamide (dmf; 0.36 ml; freshly distilled) were placed in a borosilicate glass tube (1.2 × 25 cm) which was then constricted by heating near the open end to give a short length of capillary (internal diameter ~0.2 cm) about 8 cm long. Tritiated water (1.0 ml; 21 Ci per ml, 376 mCi per mmol; provided by the Lawrence Radiation Laboratory, University of California, Livermore, Calif.) was added and the mixture of reagents was cooled to −80°C. The tube was evacuated, sealed *in vacuo* at the capillary section, and heated at 100°C. Some resin separated after 0.75 hr. After heating for 4 hr,

the tube was opened, sodium chloride was added, and the tritiated (+)-pyrethrolone was extracted with benzene (4 × 0.3 ml). The benzene solution was passed through a short column (0.6 × 2.5 cm) of anhydrous sodium sulfate, evaporated with gentle warming (<50°C), and dehydrated by pumping for 0.75 hr at 0.001 mm. The ^{3}H-(+)-pyrethrolone in benzene (1 ml) was treated with the chloride of (+)-*trans*-chrysanthemic acid (Elliott and Janes, 1969) (0.112 g; 0.6 mmol) and pyridine (60 μl) for 12 hr at 25°C in the dark; this reaction mixture was then transferred with hexane (4 ml) to a Florisil column and chromatographed (standard conditions). Only one major radioactive fraction, eluted with 25–40% ether in hexane, was obtained; fractions in this region with less than 10% of the total radioactivity were rejected. All fractions taken in this region contained only a single component other than the solvent (determined by tlc in ether–hexane mixture, then by uv visualization, or by the phosphomolybdic acid chromogenic reagent, or by radioautography). The radioactive fractions and hexane rinses (2 × 2.5 ml) of each fraction tube were combined in a conical separatory funnel fitted with a PTFE (greaseless) tap and concentrated to a volume of 20 ml in a stream of nitrogen in subdued light. The concentrate was then passed from the separatory funnel through the tap into a weighed conical centrifuge tube, evaporated under nitrogen, and freed from solvent by pumping in the dark at 0.001 mm for 0.75 hr. After weighing, the radioactive ester (0.100 g, 50%; 675 mCi per mmol) was dissolved in hexane (250 ml), and aliquots (5 ml) were sealed in ampoules under nitrogen and stored in the dark at −40°C. A second radioactive fraction, eluted from the Florisil column with ether, was (+)-pyrethrolone (10 mg) (identical with the known compound by tlc and nmr).

The radiochemical purity of the ester was greater than 98%, as determined by tlc cochromatography using either ether–hexane (2:1) or benzene–hexane–methanol (3:1:1) mixtures. Similar results were obtained immediately after preparing the ester and after storing for 1 year. When chromatography was done in light, there was evidence of very rapid photodecomposition.

^{3}H-Pyrethrin II. (II, ^{3}H at X). By a procedure similar to that for pyrethrin I, the ^{3}H-(+)-pyrethrolone from (+)-pyrethrolone hydrate (0.111 g, 0.6 mmol), potassium carbonate (0.012 g), dmf (0.33 ml), and tritiated water (1.0 ml; 21 Ci per ml) was treated with pyrethric acid chloride (0.150 g, 0.65 mmol; Elliott and Janes, 1969) and pyridine (55 μl) in benzene (1.5 ml) to give ^{3}H-pyrethrin II (0.095 g, 45%, 626 mCi per mmol) eluted from Florisil with 45–60% ether in hexane. The purity of this ester was greater than 98%, determined as with pyrethrin I, and, in light, it also underwent rapid photodecomposition.

^{3}H-Allethrin. (I, ^{3}H at X). Similarly, the ^{3}H-(+)-allethrolone from (+)-allethrolone (0.101 g, 0.66 mmol; Yamamoto and Casida, 1968), potassium carbonate (0.011 g), and tritiated water (1.0 ml, 9.3 Ci per ml) (dmf unnecessary) was treated with the chloride of (+)-*trans*-chrysanthemic acid (0.135 g) and pyridine (66 μl) to give ^{3}H-allethrin (0.12 g, 60%, 317 mCi per mmol) eluted from Florisil with 25–35% ether in hexane.

Stability of (+)-Pyrethrolone to Reaction Conditions. (+)-Pyrethrolone hydrate (0.203 g) was added to water (2 ml) containing potassium carbonate (0.023 g) and dmf (0.60 ml). In 1-cm cells this solution showed an optical rotation of +0.26°. The solution was sealed *in vacuo* and heated at 100°C for 4 hr. After 12 hr at 25°C the solution was passed through a Celite column (1 × 6.8 cm) to remove turbidity due to a trace of gum (polymerized pyrethrolone). The measured optical rotation of the eluted solution was +0.25°. Also, the uv and nmr spectra of the product were identical to those of the unheated material.

RESULTS AND DISCUSSION

Before investigating the introduction of tritium into (+)-pyrethrolone (IV, X = H) by exchange with tritium oxide, the reactivity of the cyclopentenolone nucleus was examined by observing the action of deuterium oxide on the related cyclopentenolone, (±)-allethrolone, which, unlike pyrethrolone, is obtainable commercially and conveniently soluble in water and deuterium oxide. Because no co-solvent was necessary, reactions could be studied directly without interfering media obscuring selected regions of the nmr spectrum.

Nmr spectra of deuteroallethrolone prepared by heating allethrolone for 16 hr at 150°C with deuterium oxide (sealed tube) or for approximately 10 min at 100°C in the presence of 1% potassium carbonate established that only protons on the methylene group adjacent to the carbonyl and on the methyl group had been exchanged for deuterium. Although there are many precedents for exchange of the methyl and methylene protons adjacent to carbonyl groups (Fetizon and Gramain, 1969), proton exchange in a methyl group on this cyclopentenolone nucleus has not been observed before. All labile protons were almost completely replaced by deuterium after two successive treatments with deuterium oxide containing potassium carbonate (1%). The nmr spectra (Figure 2) of the starting material, (±)-allethrolone, and the deuterated product show that the signals due to the olefinic side chain protons at τ 4.3 (m) and τ 5.2 (complex) and the side chain methylene at τ 7.02 (d) were unchanged after deuteration. The most prominent differences were the disappearance of the methyl resonance (singlet) at τ 7.97 and the two methylene protons adjacent to the carbonyl group seen as double doublets (*J* values 6 and 18 and 2 and 18 Hz, respectively) at τ 7.2 and 7.8. Most significantly, the proton (τ 5.4) of the asymmetric carbon atom at C-4 of the cyclopentenolone ring was not displaced, but the nature of its signal changed because the protons to which it was coupled, producing the diffuse doublet in the undeuterated sample, were removed.

After one treatment of allethrolone with deuterium oxide containing 1% potassium carbonate, some unsubstituted methyl group remained. As expected, the mass spectrum showed that, of this product, 64% was $^2H_4$ species, 29% $^2H_3$, and only 7% $^2H_5$, in agreement with an estimate from the nmr spectrum by the integram of the area under the methyl peak at τ 7.97. A second treatment with deuterium oxide and potassium carbonate gave a product shown by nmr to contain only a very small proportion of molecules without fully deuterated methylene and methyl groups. The mass spectrum of this deuterated allethrolone agreed completely with the structure indicated by nmr. Thus, the deuterated and undeuterated components showed: molecular ions (M^+) of 157 and 152, respectively; ions at 139 and 137 for the parent fragments resulting from elimination of C^2H_3 and CH_3 groups, respectively, with the mass difference of 2 units because of the fully deuterated methylene position. Other ions (*m/e* 129 and 124) came from elimination of CO, leaving all five deuterium atoms substituted in the fragment from the deuterium-labeled material. The deuterated compound showed M^+ of 157, not 158, the most labile deuterium ($-O^2H$) having obviously been exchanged with hydrogen from water in the inlet system of the mass spectrometer.

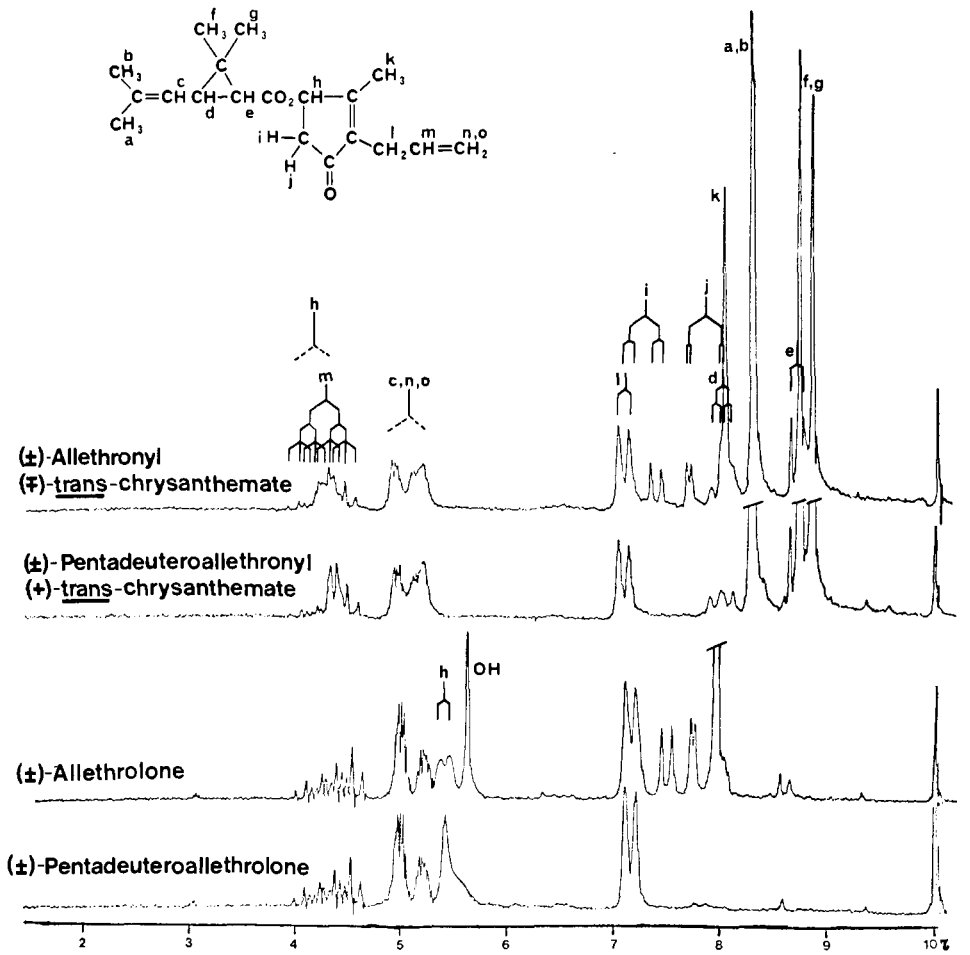

Figure 2. Nuclear magnetic resonance spectra of allethrolone, deuteroallethrolone, allethrin, and deuteroallethrin, in carbon tetrachloride, with assignments

Even the twice deuterated product was seen by nmr to be approximately 50% O*H* (Budzikiewicz *et al.*, 1964).

Examination of deuterated compounds gave an indication of the stability expected for equivalently-substituted tritiated products. The nmr spectrum of pentadeuteroallethrolone (Fig. 2) showed that none of the five protons was displaced when a benzene solution of the deuterated compound was washed with saturated sodium chloride solution. Further, no deuterium was lost in water at neutral pH after 49 days at 25°C. The pentadeuteroallethrin (Fig. 2) prepared under usual esterification conditions from the chloride of (+)-*trans*-chrysanthemic acid in benzene with pyridine showed an nmr spectrum confirming all the five deuterium atoms; in the region of τ 7.9 a double doublet from the proton on C-3 of the cyclopropane ring trans to the carboxyl group was plainly evident, although in allethrin the signals from this proton are obscured by those from the methylene position. Because the allethrolone used for deuteration experiments was racemic [(±)], the product with the chloride of (+)-*trans*-chrysanthemic acid was a mixture of two diastereoisomers, each of which gave, as previously discussed (Bramwell *et al.*, 1969), almost identical spectra except for the 4-C*H* proton at the center of asymmetry on the cyclopentenonyl ring. In (±)-pentadeuteroallethronyl (+)-*trans*-chrysanthemate (Fig. 2), splitting from the 5-CH_2 is absent and the 4-C*H* signals are sharpened singlets, not broad doublets, as in undeuterated allethrin isomers, and appear distinctly separated at τ 4.31 and 4.37. In a prolonged esterification trial, the pentadeutero alcohol and acid chloride were left in benzene solution in the presence of the separated pyridine hydrochloride for 19 days. The nmr spectrum again showed the complete absence of resonances at τ 7.1 and 7.8 for the methylene protons and at τ 7.97 for the methyl group. These experiments indicated that the tritiated compound would be unlikely to lose tritium under esterification conditions.

Mass spectral evidence also confirmed the structure of the pentadeutero ester. The molecular ion (M^+) at 307 had an intensity approximately nine times greater than that of the peak at *m/e* 306, confirming that 90% of the ester was pentadeuterated. Both the pentadeutero ester and allethrin showed peaks at *m/e* 168 (chrysanthemic acid, $C_9H_{15}CO_2H$), at 123 and 153 ($C_9H_{15}CO_2H - CH_3$). Fragments *m/e* 141 and 136 from the pentadeutero compound and allethrin, respectively, differed by 5 mass units and so originated from the allyl methylcyclopentenonyl ring, probably by a rearrangement involving fission of the *O*-carbon bond and simultaneous transfer of a hydrogen atom (from the acid) on to the carbonyl oxygen. Further fragments (112 and 107) came from those of *m/e* 141 and 136, respectively, by loss of CHO (29).

Some differences in procedure were necessary when (+)-pyrethrolone was substituted for allethrolone in the exchange reactions. Although all labile protons in allethrolone were completely exchanged in about 10 min at 100°C with deuterium oxide of 99.5% isotopic purity, in the presence of 1% potassium carbonate, theoretical considerations indicated that the exchange reaction with tritiated water of even the highest specific activity available (containing about 1% tritiated molecules) would be much slower to reach equilibrium. Another complication was the insolubility of (+)-pyrethrolone in water and in deuterium oxide, so that a cosolvent was necessary to produce a homogeneous reaction

medium; about 30% of dmf was convenient for this purpose. In preliminary experiments, the specific activity of (+)-pyrethrolone was measured after heating for various periods with tritium oxide containing 1% potassium carbonate and one third volume of dmf; the exchange had not reached equilibrium after 4 hr. A reaction period of 24 hr was investigated using water of 8.0 mCi per mmol and it was found that pyrethrin I prepared from (+)-pyrethrolone equilibrated for this period had almost the full specific activity ($5 \times 8/2 = 20$ mCi per mmol) theoretically attainable (Table I). However, especially with tritiated water of the greatest specific activity available (20 Ci per ml), heating for longer than 4 hr gave larger quantities of polymer from (+)-pyrethrolone (but not from allethrolone), possibly because of the peroxide content of such active tritiated water (Evans, 1966). Equilibration for 4 hr at 100°C was therefore a suitable compromise for the heating period. Separate experiments with water showed directly that (+)-pyrethrolone was not racemized or modified in other ways by such heating. Also, in confirmation that pyrethrolone, like allethrolone, was unaffected by the conditions used for equilibration with tritium oxide, a small quantity of this starting material was recovered from the reaction mixtures in the ^{3}H-ester syntheses. It was concluded, therefore, that in (+)-pyrethrolone only protons on the nucleus in positions equivalent to those labile in allethrolone would be replaced by tritium. In four independent determinations it was shown that after 3.25–4 hr the specific activity of the products was 67–78% of that theoretically attainable and that, for all practical purposes, esters prepared from (+)-pyrethrolone exchanged with tritium in this way would be uniformly labeled at all five exchangeable positions to about 70% of the theoretical level (Table I).

For synthesis of tritiated esters, therefore, (+)-allethrolone (without additional solvent) or (+)-pyrethrolone (with dmf to give a homogeneous reaction mixture) was heated with high specific activity tritiated water containing 1% potassium carbonate at 100°C for 4 hr. Labeled alcohols were displaced from the reaction media with sodium chloride, isolated, and esterified, either with the acid chloride of naturally-derived (+)-*trans*-chrysanthemic acid or with that of (+)-pyrethric acid (Elliott and Janes, 1969). The esters were purified on chromatographic columns and stored as dilute solutions in hexane. Radiometric tlc assays showed that, when the chromatograms were developed in the dark, at least 98% of the radioactivity was in the active esters, with R_f values identical with those of authentic samples. Much photodecomposition and subsequent tailing of the spots occurred when the compounds on the tlc plates were exposed to light. Apparently, any exchange of tritium from the esters in biological systems is slow enough not to limit their use for metabolism studies. These tritiated esters have been used successfully to characterize products from metabolism by enzymatic preparations and living mammals, where the positions labeled were not those attacked (Casida *et al.*, 1971; Elliott *et al.*, 1972). Further, the positions labeled seem not to be involved in the biological activity of the pyrethroids because little difference in toxicity to houseflies or mustard beetles was found (Farnham and Needham, 1970) between allethrin and pentadeuteroallethrin. This is important because it indicates that the tritiated esters might be useful for locating the binding site in nerve tissue involved in pyrethrin-like activity.

This new method for radiosynthesis of pyrethroids that contain the cyclopentenonyl ring has distinct advantages over procedures previously available in the simple manipulations involved and the high specific activities attained.

Table I. Specific Activities of Pyrethrin I, Pyrethrin II and Allethrin Prepared from (+)-Pyrethrolone and (+)-Allethrolone Equilibrated with Tritium Oxide for Varying Periods

Ester prepared	^{3}HOH used, mCi/mmol	Time of equilibration for the alcohol, hr	Specific activity		
			Theory	Found	% of theory
Pyrethrin I	8.0	3.25	20	15.6	78
Pyrethrin I	8.0	24	20	19.3	97
Pyrethrin I	376	4	940	675	72
Pyrethrin II	376	4	940	625	67
Allethrin	166	4	415	317	76

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