

made using BHC in 1951 and 1952.

2. The chemical, which was produced by benzene hexachloride (γ content: 1%), was composed in the Laboratory of Agricultural Chemicals, Kyoto University. The treated azuki bean (*Phaseolus angularis* W. F. Wight.), which is var. DAINAGON, was produced at Settu Experimental Farm, Kyoto University.

3. Applying 5cc of 1% γ -BHC trichloro-

ethylene benzene solution per To (0.5 bush.) of azuki bean seeds, the controlling effect is very good to azuki bean weevil.

4. This insecticidal liquid (γ -BHC: 1%) has strong insecticidal activity to azuki bean weevil, and moreover the germination of azuki bean seeds is normal in the case treating with BHC.

Polarographic Determination of Allethrin. 1. (Studies on Determination of Pyrethroids. I.) Toshihiko OIWA, Yuzo INOUE, Jiyouzo UEDA, and Minoru OHNO (Takei Laboratory, Institute for Chemical Research, Kyoto University) Received Sept. 8, 1952. *Botyu-Kagaku*, 17, 106 (1952).

21. アレスリンのポーラログラフ法による定量. 1. (ピレトリン類縁物質の定量に関する研究. 第1報) 大岩俊彦, 井上雄三, 植田穰三, 大野 稔 (京都大学化学研究所 武居研究室) 27. 9. 8 受理

最近 pyrethroids の化学が長足の進歩を遂げ、その一種である allethrin は工業的に合成され、やがて広く一般に使用されようとしている。allethrin の定量法としては、夫々の分野から、S. Hestrin 等⁽¹⁾、J. B. Moore⁽²⁾、F. B. LaForge 等⁽³⁾ 及び山田等⁽⁴⁾ の提案がある。前二者の方法は原理的にも疑点があると共に、操作がやや繁雑である。山田等の方法はポーラログラフ法によるもので、pyrethroids の定量に始めてこの方法を採用した点は特筆されるべきであるが、基礎的な検討が不足していると思われる。最近、たまたま LaForge 等⁽³⁾ は、融点 50.5~51° の allethrin の一異性体 (α -dl-trans-allethrin) を結晶状に単離した。著者等もこれにならつて、この異性体を単離し、これを標準試料として allethrin のポーラログラフ法による定量の研究を行つた処、満足すべき結果を得たので、まだ多くの検討すべき点もあるが茲に発表して大方識者の批判を仰ぐ次第である。此の方法の利点として特に強調したいことは次の二つである。即ち第一には allethrin をエステル形のままで直接定量することによつて精度を上げること、第二にはこの様な物理的手段の採用によつて、操作が簡易迅速化されることである。

α -dl-trans-allethrin を水銀滴下電極で、山田等が用いたのと同じ組成の電解液 [ethyl alcohol (50%), $M/5$ (CH_3)₄NBr 溶液 (10%), 緩衝液 (40%)] 中で還元した処、典型的な還元波が得られた。この組成で、Table 2 に示す種々の pH の緩衝液を用い、 $25 \pm 0.2^\circ$ でポーラログラムを撮つた処、Fig. 1~4 に示す様に種々の還元波を得た。これらの各種

の還元波を種々の点で比較検討し、分析に最適な緩衝液の pH は 3.0 附近であることを知つた。pH 2.96 の Sørensen 緩衝液を用いた場合の電解液の pH は約 4 であり、半波電位 (N -甘汞電極基準) は約 -1.27 v. であつた。

次にこの pH 2.96 の場合に於て、 α -dl-trans-allethrin の還元波に及ぼす温度の影響を検討した処、温度の上昇と共に半波電位は負に移行し、又波高は Fig. 5 及び式 1 に示す様に直線的に増加した。5° から 30° の間の波高の温度係数は、約 2.7% (5°) から約 1.6% (30°) である。従つて 25° 附近で温度の影響に基く誤差を $\pm 1\%$ 以内に留めるには、還元温度を少くとも $\pm 0.5^\circ$ 以内に保つ必要がある。著者等の定量法では $25 \pm 0.5^\circ$ に規定する。

pH 2.97 の緩衝液を用い、上述の電解液組成で、 $25 \pm 0.2^\circ$ に於て、 α -dl-trans-allethrin の種々の濃度に於ける波高を測定した処、その関係は Fig. 6 及び式 3 に示す様に、座標軸の原点を通る直線で表わされた。従つて此の関係式を用い、逆に波高から電解液中の α -dl-trans-allethrin の濃度を知ることができる。

一般に、立体異性体中光学異性体のポーラログラムは同一であるが、幾何異性体間では異なる場合がある。allethrin には 16 の理論立体異性体が考えられるが、幾何異性体としては、所謂 cis 及び trans の二種である。分別クロマトグラフ法によつて精製した dl-cis, trans-, dl-cis- 及び dl trans-allethrin のポーラログラムを α -dl-trans-allethrin と同一の条件で撮つた処、Fig. 7 及び Table 1 に示す様に、波形、半波電位及び濃度と波高の関係の何れも同一であつた。

従つて単離し易い α -dl-trans-allethrin を allethrin のポーログラフ分析の基準物質としてさしつかえない。

以上の諸結果を考慮して、allethrin の分析操作を次の様に決めた。60 mg 内外の試料を、10 cc のメスフラスコに正確に秤取し、ethyl alcohol を加えて 10 cc にする。この原液 1 cc を栓付試験管に秤取し、これに ethyl alcohol 4 cc と $M/5$ $(CH_3)_4NBr$ 液 1 cc を加え、次に pH 2.97 の Sørensen の緩衝液 4 cc を加える。振盪後、陽極水銀を入れて予め 25° 附近に調節してある電解瓶に入れる。直ちに水素を通じて混在する酸素を追い出す。緩衝液を加えてから 30 分後に、水素の通入を止めて $25 \pm 0.5^\circ$ でポーログラムを撮る。allethrin の含量が 25% 以下の工業製品になると、混在する不純物のために一般に還元波が不明瞭となり、作図が困難となる。この様な試料では、電解瓶中に一定量の α -dl-trans-allethrin の純品を特に加えて、明瞭な波形の還元波を得る様にする。かくして得たポーログラムは Fig. 8 に示す作図法に従い波高を測定し、同様な操作を行つて作成した α -dl-trans-allethrin の純品の濃度と波高の関係式(式 3)から allethrin の含量を求める。

この方法の精度を知るために次の様な検討を行つた。allethrin 製品に夾雜してくる可能性のある中間原料或は近縁物質である dl-allethrolone (I), 3-hydroxy-8-nonene-2,5-dione の dl-cis, trans 第一菊酸エステル(粗品; II), 3-hydroxy-8-nonene-2,5-dione (粗品; III), ethyl-3-oxo-6-heptenoate (IV), allyl acetone(V), pyruvaldehyde(VI), 及び dl-cis-(VII) 及び dl-trans-第一菊酸(VIII)のポーログラムを上述と同じ条件で撮つた。dl-allethrolone のポーログラムは Fig. 9 の I に示す様で、その半波電位 (N -甘汞電極基準) は約 -1.45 v. であり、allethrin の半波電位より約 0.2 v. 負である。 α -dl-trans-allethrin 中に dl-allethrolone が

入ると Fig. 9 の II 及び III に示す様に allethrin の拡散電流の傾斜が立つてくる。そして dl-allethrolone がある量以上になると明瞭に 2 段波を示した。この様に拡散電流の傾斜が立つために、上述の作図法によつて allethrin 量を求めると、幾分か低い値が得られる。此の場合の誤差は Table 8 に示す様に、dl-allethrolone の量が allethrin と同モルの場合で -7.5%, 1/2 モルの場合で -6.2%, 又 1/4 モルの場合で -4.4% であつた。(II)~(VIII) の物質のポーログラムは Fig. 10 及び 11 に示す様で -0.1 から -1.6 v. の間では何れも還元波を示さない。然し乍ら allethrin の還元波に影響を与えることも考えられたからこれらの物質を適当に調合した種々の合成試料をつくり、その中の α -dl-trans-allethrin を定量した。その結果は、Table 7 及び 9 に示す様で、実際に工業製品中の allethrin を定量する場合に、これらの物質の影響を考慮する必要は先ずない。

次に製造者のことなる種々の allethrin の工業製品を、上述の方法で定量した。今その一例を示す。得られたポーログラムは Fig. 15 及び 16 に示す様で、何れも作図が可能な波形であつた。夫々の定量結果は Table 10 に示す様である。更にこれらの製品に一定量の α -dl-trans-allethrin の純品を加え定量した処、添加 α -dl-trans-allethrin 量と定量値とは Table 10 に示す様に良く一致した。

以上の事から、著者等がこの提案する定量法で、工業製品を定量する際生ずる誤差は、大部分の試料では、実験誤差内と考えてよい。然し乍ら未反応 dl-allethrolone が多量に含まれている試料ではやゝ低い値となる。これの補正に就いては目下検討中で、追つて発表する。

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It is remembered that the staff of this laboratory has made investigations on the chemical estimation of the effective constituents in the natural pyrethrum flower. The present authors intended to investigate the determination of the natural and synthetic pyrethrins from the standpoints (1) of determining pyrethrins without breaking the ester form to obtain as accurate values as possible for biologically active material, and (2) of increasing the efficiency of the analysis by adopting such physical methods as polaro-

graphy and spectrophotometry. This report describes the determination of allethrin by polarographic method.

A remarkable progress has been made in recent years in the synthesis of pyrethrins. Especially, allethrin has been synthesized industrially, and has vast possibility of being put into practical use in the near future. It is earnestly desired on this juncture that a precise method of determination of allethrin in technical products, which would benefit both the study of synthesis and the practical

production, should be established as soon as possible.

S. Hestrin and K. A. Lord⁽¹⁾ described the spectrophotometric determination of coloured complex derived from allethrin, and J. B. Moore⁽²⁾ developed a method in which allethrin is reacted with hydroxylamine and the excess of the hydroxylamine is then determined by measuring its reducing effect on polyvalent metals either by titration or colorimetrically. The hydrogenolysis method (and its modification) has been proposed recently as a tentative method by F. B. LaForge et al.⁽³⁾. Although the authors have not traced these methods of analysis in comparison with the authors' polarographic method, they seem to be much complicated in procedure and their fundamental principles are not without question.

On the other hand, it has been proved recently by R. Yamada et al.⁽⁴⁾ that crude allethrins are reduced at dropping mercury cathode, that the half-wave potential is about -1.25v. , and that the relation between the concentrations and the wave heights can be represented by a linear equation. They, as a result of these experiments, indicated the possibility of analysing allethrin quantitatively by the polarographic method. They, however, made no investigation on a pure isomer of allethrin and neither they referred to the determination of allethrin in technical allethrin.

The currently used methods of analysis for standardization of pyrethrum products are Seil's and mercury reduction methods. The authors' experiences have proved Seil's method not applicable to technical allethrin. The application of mercury reduction method to allethrin seems of little meaning in principle, although it has not been actually applied by the authors.

It is reported that F. B. LaForge et al.⁽⁵⁾ recently succeeded in separating an isomer of allethrin (α -dl-trans-) as pure crystals, which melts at $50.5\sim 51^\circ$. With this pure crystalline isomer as standard material, the authors' investigation of determining allethrin was carried out by polarographic method. This method gave the reliable and satisfactory results, and is believed

more convenient and less time-consuming than those methods mentioned above.

I. POLAROGRAM OF α -dl-trans-ALLETHRIN

1. Preparation of Supporting Electrolyte Solution.

The composition of the supporting electrolyte solution was the same as in the case by R. Yamada et al.⁽⁴⁾, and is as follows:

Ethyl alcohol (50%), and $M/5(\text{CH}_3)_4\text{NBr}$ solution (10%), and buffer solution (40%).

As stated in later paragraphs, the typical reduction wave can be obtained in this composition of the supporting electrolyte solution. It is also seen when dioxane is used as solvent, instead of ethyl alcohol.

2. Influence of pH on Reduction Wave.

The polarograms of α -dl-trans-allethrin were taken, with the aid of various buffer solutions, by the method and under the conditions described in I of III. The result is shown in Fig. 1~4. The values of pH in the figures are

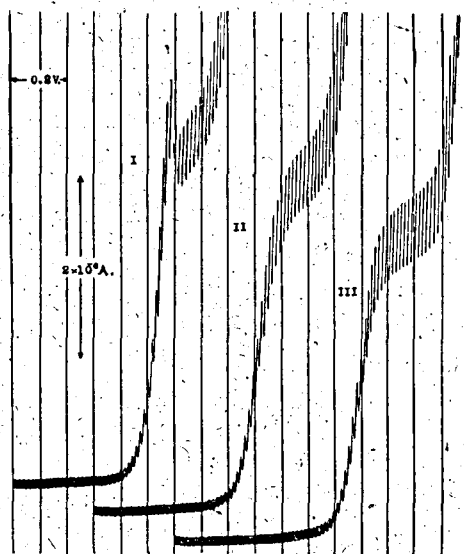


Fig. 1: Polarograms of $16 \times 10^{-4} M$ α -dl-trans-allethrin reduced at different pH values: I (pH 1.15) begins at -0.57 v. II (pH 2.15) begins at -0.57 v. III (pH 2.96) begins at -0.58 v.

of the buffer solution added. The wave forms were different when pH was 1.15, 2.15, 2.96, and 3.97, although the polarograms in every

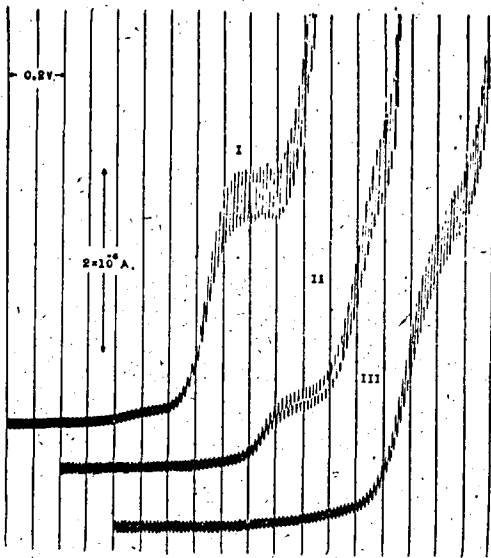


Fig. 2: Polarograms of $16 \times 10^{-4} M$ α -di-trans-allethrin reduced at different pH values: I (pH 3.97) begins at -0.57 v. II (pH 5.01) begins at -0.56 v. III (pH 5.95) begins at -0.57 v.

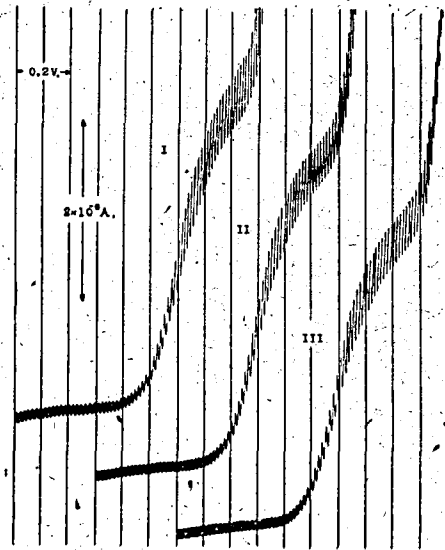


Fig. 4: Polarograms of $16 \times 10^{-4} M$ α -di-trans-allethrin reduced at different pH values: I (pH 10.12) begins at -1.12 v. II (pH 10.86) begins at -1.13 v. III (pH 12.12) begins at -1.15 v.

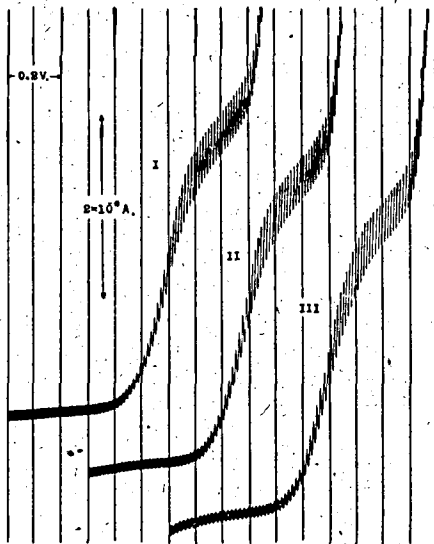


Fig. 3: Polarograms of $16 \times 10^{-4} M$ α -di-trans-allethrin reduced at different pH values: I (pH 6.90) begins at -1.07 v. II (pH 8.14) begins at -1.09 v. III (pH 9.19) begins at -1.10 v.

case showed one-step reduction. As the value of pH increased, the reduction potential*

* The potential in this report is shown by N-Calomel Electrode Standard.

shifted to the negative by degrees, and the wave height decreased. When pH was 1.15, the maximum appeared. When pH was 2.96, pH of the electrolytic solution itself was about 4, and the half-wave potential was about -1.27 v.

When pH was 5.01, the polarogram showed two-step reduction and it is supposed that the first wave was due to the reduction mechanism stated above, and the second wave, to the reduction mechanism when pH was below 5.95. The wave form and the wave height in this polarogram did not change by time.

When pH was 5.95, 6.90, 8.14, 9.19, 10.12, 10.86, and 12.21, the polarograms again showed one-step reduction, but the wave forms in these were different from the ones in the cases stated above, and the reduction potentials went fast into the negative. Among these cases, however, the differences of wave form, and wave height were not very great, and the reduction potential shifted a little to the negative by degrees as the value of pH increased.

The change in the mode of reduction from one step to two steps, and again to one step

according as the value of pH changed, appeared very often in the reduction at the dropping mercury electrode of the compounds with ketone radical. The authors, after carefully comparing those polarograms, and considering the easiness or difficulties in measuring wave height in respective cases, chemical stability in the electrolytic solution, and other elements, decided that the value of pH of the buffer solution used suitable for the analysis is 3.0 or thereabout.

3. Effect of Temperature on Reduction Wave.

The temperature is highly influential in polarographic analysis. As to how the temperature affects the diffusion current, D. Ilkovič, I.M. Kolthoff and J.J. Lingane⁽⁶⁾, have pointed out that, as the temperature rises, the diffusion coefficient of the reductant increases, and the dropping mercury becomes less viscid and easier to drop, and, together with other elements, cause the diffusion current to go up.

The polarograms of α -dl-trans-allethrin were taken at various degrees of temperature by the method shown in 1 of III, while the concentration and the composition of the electrolytic solution were kept constant. The wave height increased linearly in proportion to the increase of temperature, as shown in Fig. 5.

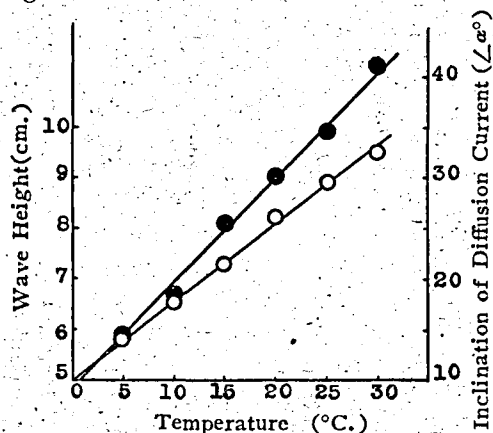


Fig. 5: Wave heights and inclinations of diffusion current of $16 \times 10^{-4} M$ α -dl-trans-allethrin at different temperatures: O, indicates wave height (1mm wave height = $3.09 \times 10^{-8} A.$); ●, indicates inclination of diffusion current.

The theoretical equation of the curve is as below.

$$id = 0.158 T + 5.08 \dots \dots (1)$$

In this equation id shows the wave height in centimeters and T signifies the temperature in Centigrade. Under these circumstances, therefore, the positive temperature coefficients of wave height varied between about 2.7% at 5°C. and about 1.6% at 30°C.

As shown in Fig. 5, the inclination of diffusion current ($\angle \alpha$) increased linearly as the temperature rose. On the other hand, the half-wave potential went gradually into the negative as the temperature rose.

Consequently, from the analytical viewpoint, it is evident that the temperature should be controlled to at least $\pm 0.5^\circ C.$, or better, in order to keep errors due to the temperature effect within $\pm 1\%$, when the temperature is $25^\circ C.$ or thereabout.

4. Relation between Concentrations and Wave Heights.

By the method and under the conditions described in 1 of III, the relation between the concentrations and the wave heights of α -dl-trans-allethrin was studied, and the result obtained is shown in Fig. 6.

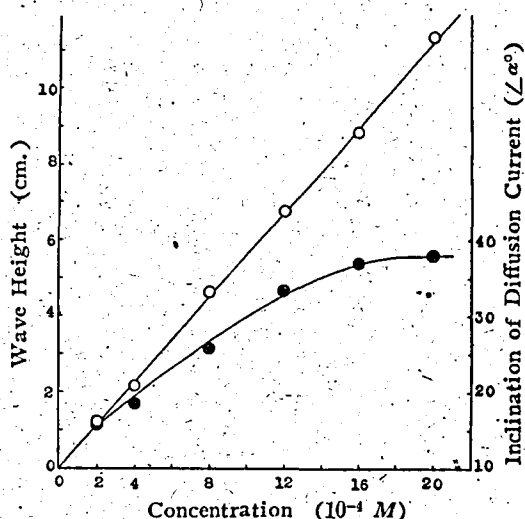


Fig. 6: Wave heights and inclinations of diffusion current of $16 \times 10^{-4} M$ α -dl-trans-allethrin at different concentrations: O, indicates wave height (1mm. wave height = $3.09 \times 10^{-8} A.$); ●, indicates inclination of diffusion current.

The standard theoretical equation obtained crosses the axis of coordinates at zero point, and is as below.

$$id_1 = 0.563C_1 + 0.019 \dots\dots(3)$$

where, id_1 is the wave height in centimeter, and C_1 is the concentration shown in unit of $10^{-4}M$. Therefore, the wave heights are proportional to the concentrations and the calculated values and experimental values are almost the same, with possible experimental errors considered. Conversely, therefore, the concentration of α -dl-trans-allethrin in the electrolytic solution can be calculated precisely from the wave height.

The inclination of diffusion current, as shown in Fig. 6, increased exponentially as the concentration increased.

The change by time of the reduction wave under the conditions described in I of III was studied. Neither the wave form nor the wave height showed any change after 12 hours at $25 \pm 0.2^\circ C$.

II. POLAROGRAM OF THE GEOMETRICAL ISOMERS OF ALLETHRIN

When the geometrical structure of stereo isomers is different, the reduction wave, in most cases, appears different as is known, but the optical isomers show the same reduction wave. Now, if the cyclopentenone ring is a plane, there are theoretically 16 isomers possible for allethrin, but among these, the two geometrical isomers, which are due to the cis and trans configurations of chrysanthemum monocarboxylic acid, are investigated here.

The polarograms were taken of dl-cis, trans, dl-cis, and dl-trans isomers of allethrin by the method and under the conditions described in I of III. In all cases, the wave form and the reduction potential are identical with those of α -dl-trans-allethrin as shown in Fig. 7. The half-wave potentials and the relations between the concentrations and the wave heights are shown in Table I.

It is safely, therefore, surmised that the relation between the concentrations and the wave heights in the case of α -dl-trans-allethrin represent that of the other isomers of allethrin. Consequently, it is wise that α -dl-trans-allethrin, which can easily be obtained as pure

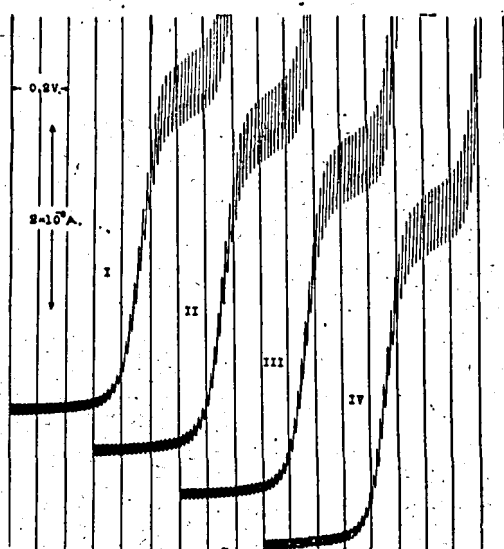


Fig. 7: Polarograms of geometrical isomers of allethrin: I (α -dl-trans), II (dl-cis, trans), III (dl-cis), IV (dl-trans). Each concentration is $16 \times 10^{-4}M$, and each polarogram begins at -0.80 v.

Table I: Half-Wave Potential and Relation between Concentrations and Wave Heights of Geometrical Isomers of Allethrin.

Isomer of Allethrin	Half-Wave Potential v.	Relation between Concentrations and Wave Heights
α -dl-trans	ca. -1.27	$id_1 = 0.563 C_1 + 0.019$
dl-cis, trans	ca. -1.27	$id_2 = 0.550 C_2 + 0.030$
dl-cis	ca. -1.27	$id_3 = 0.547 C_3 + 0.044$
dl-trans	ca. -1.27	$id_4 = 0.564 C_4 - 0.120$

crystals, should be used as standard matter of the polarographic determination of the total isomers of allethrin.

III. QUANTITATIVE DETERMINATION OF ALLETHRIN

The following is the method of determination of allethrin devised after the above-mentioned investigations, and the study of the accuracy of this method with various samples.

1. Method of analysis.

a. Apparatus. In quantitative analyses, generally, the multiplying power of the galvanometer shunt is adjusted, and the coefficient is determined for the later calculation. In the case of allethrin, however, the difference in the multiplying power results in the difference of the wave form, which causes

errors in the construction. It is recommended, therefore, that the multiplying power is kept constant, and the samples are taken in such a way that the allethrin concentration in the electrolytic solution is kept within the given range in all cases. Furthermore, the wave form differs with the characteristics of the galvanometer, which necessitates the experimenter to be well experienced with the apparatus.

The electrolytic cell is of the same type as used by M. Nakazima et al.⁽⁷⁾ in quantitative analysis of BHC. This cell can keep the temperature of electrolytic solution constant easily.

b. Reagents.

The reagents must have undergone a blank test and shown no reduction waves. It is necessary that this blank test should be done every time the reagent is used.

1) *Ethyl Alcohol*: Ethyl alcohol of bp. 78° from which aldehydes have been completely removed in the undermentioned way is used. Conc. sulphuric acid and water is added to alcohol (Proportion: H_2SO_4 5 cc., H_2O 20 cc., alcohol 1 litre), and distilled. To the distillate, silver nitrate and potassium hydroxide are added (Proportion: AgNO_3 10 g., KOH 1 g., the distillate 1 litre), and after several hours' boiling is redistilled.

2) *M/5((CH₃)₄NBr) solution*: Tetra-methyl ammonium bromide is purified by recrystallization from alcohol, and dissolved into distilled water.

3) *Buffer solution*: Sørensen's sodium citrate-hydrochloric acid buffer solution of pH 2.97.

4) *Hydrogen*: Oxygen is completely removed beforehand by passing it through at least five pyrogallol washing bottles (10 g. of pyrogallol is dissolved into 100 cc. of saturated KOH or NaOH solution).

5) *Mercury*: Mercury used at cathode and anode has been purified by distillation, after being washed with nitric acid solution.

c. Procedure.

1) *Sample with Allethrin Content above about 25%*.

About 60 mg. of sample (weight must be mea-

sured accurately) is placed in 10 cc. measuring flask, and is made up to 10 cc. with ethyl alcohol. One cc. of this stock solution is taken in a test tube carrying a glass stopper, added with 4 cc. of ethyl alcohol and 1 cc. of $\text{M/5}(\text{CH}_3)_4\text{NBr}$ solution. To this solution, 4 cc. of buffer solution is added, shaken, and poured into the electrolytic cell which has been contained anode mercury, and of which temperature kept at $25 \pm 0.5^\circ\text{C}$. When the procedure is over, dissolved oxygen is removed from the solution at $25 \pm 0.5^\circ\text{C}$. by a stream of hydrogen (too strong a rush of hydrogen may cause the electrolytic solution to evaporate). Thirty minutes later, after the buffer solution is added, hydrogen is cut off, and the polarogram is taken at $25 \pm 0.5^\circ\text{C}$.

2) *Sample with Allethrin Content below about 25%*.

As stated later, when the allethrin content in technical allethrin is below 25%, generally, the wave form is obscure, and the construction becomes difficult. If the experimenter finds out by the above-mentioned method that the sample belongs to this category, therefore, it is advisable for him to add a certain amount of pure α -dl-trans-allethrin to the electrolytic solution so that the typical wave can be obtained.

About 60 mg. of sample (weight must be measured accurately) is placed in 10 cc. volumetric flask, and is made up to 10 cc. with ethyl alcohol. One cc. of this stock solution is taken in a test tube carrying a glass stopper, and added with 4 cc. of 10^{-4}M α -dl-trans-allethrin ethyl alcohol solution, and 1 cc. of $\text{M/5}(\text{CH}_3)_4\text{NBr}$ solution. The later process is the same as in the case stated above.

The wave height of the polarogram thus obtained is measured by the construction method mentioned below. The concentration of allethrin is calculated from the measured curve (equation 3) prepared by the similar process in pure α -dl-trans-allethrin.

d. Method of Measuring the Wave Height.

The method of construction is nearly the same as the one by R. Yamada et al.⁽⁴⁾ As indicated by Fig. 8, a slope line is drawn

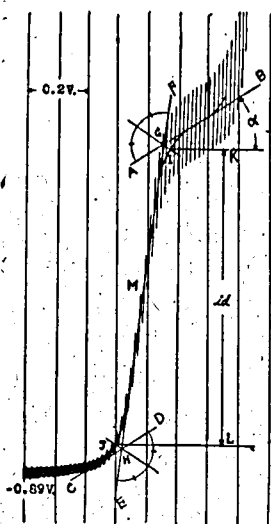


Fig. 8: Method of measuring wave height.

through the center of oscillations. A straight tangential line (AB) is drawn to the slope line in diffusion current, and another straight tangential line (CD) is drawn at the bending at the foot in parallel with the line (AB). Then, a straight line (EF) is drawn through the point of half-wave potential (M), and the points at which this line (EF) crosses the already drawn two lines (AB and CD) are marked G and H, respectively. The bisecting lines of the intersecting angles ($\angle FGA$ and $\angle DHE$) are then drawn, and the points at which those lines intersect the slope line are marked I and J, respectively. The perpendicular distance between I and J, i.e. KL, is the wave height.

Next, in order to determine the inclination of the diffusion current, the degree of intersecting angle ($\angle \alpha$) made by the line (AB) and the horizontal axis of this current-voltage curves, is determined.

2. Polarograms of Related Compounds of Allethrin and Influence of Those Compounds on Reduction Wave of α -dl-trans-Allethrin.

The result of the study on the polarograms of the intermediate substances (Sample 5~13 of 2 of Experimental Part), which might contaminate the technical allethrin in the process of its production, is as follows:

The polarogram of allethrolone taken under

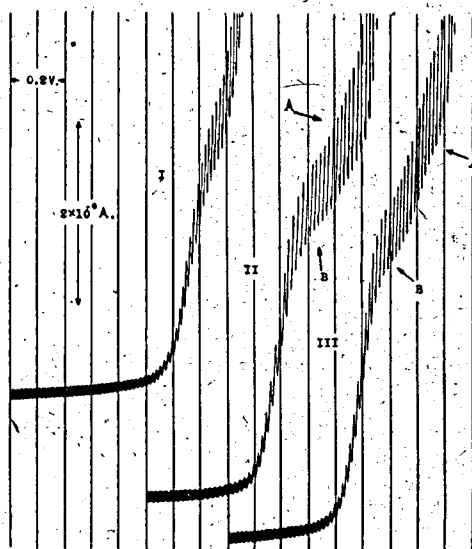


Fig. 9: Polarograms of dl-allethrolone and mixtures of α -dl-trans-allethrin and dl-allethrolone: I ($16 \times 10^{-4} M$ dl-allethrolone), II ($16 \times 10^{-4} M$ α -dl-trans-allethrin + $4 \times 10^{-4} M$ dl-allethrolone), III ($16 \times 10^{-4} M$ α -dl-trans-allethrin + $8 \times 10^{-4} M$ dl-allethrolone). Part of A indicates dl-allethrolone, and part of B indicates α -dl-trans-allethrin. Each polarogram begins at -0.79 v.

the conditions described in 1 of III is shown in 1 of Fig. 9. The half-wave potential of allethrolone was about -1.45 v., which was further in negative than that of allethrin, by about 0.2 v. The polarograms taken of the substances of Sample 6~10, 12, and 13 under the same conditions are illustrated in Fig. 10, and 11. They do not show the reduction wave between -0.1 v. and -1.6 v., but it is supposed that they may influence the reduction wave of allethrin. In this sense, many samples were prepared with those substances in various proportions, and α -dl-trans-allethrin were analysed. Ethyl-3-oxo-6-heptenoate, pyruvaldehyde, and dl-cis, trans-chrysanthemum-monocarboxylic acid have no influence at all, as shown in Table 7.

a. Influence of dl-allethrolone.

As indicated by Fig. 9, and 12 when dl-allethrolone was added to α -dl-trans-allethrin, the diffusion current of α -dl-trans-allethrin became steeper. According as the quantity of

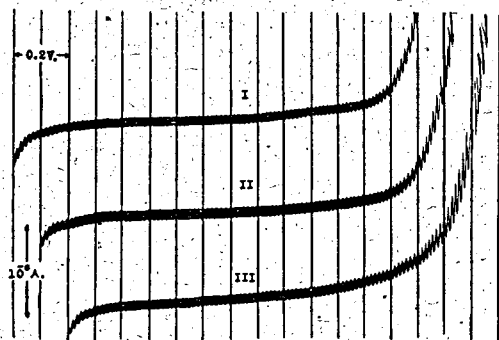


Fig. 10: Polarograms of related compounds of allethrin: I (ethyl-3-oxo-6-heptenoate), II (crude matter of 3-hydroxy-8-nonene-2,5-dione), III (crude matter of dl-cis, trans-chrysanthemum-monocarboxylate of 3-hydroxy-8-nonene-2,5-dione). Each concentration is $16 \times 10^{-4} M$, and each polarogram begins at -0.09 v.

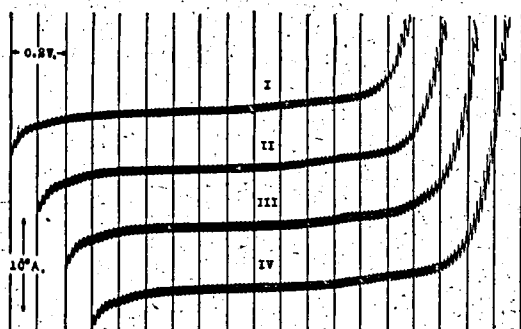
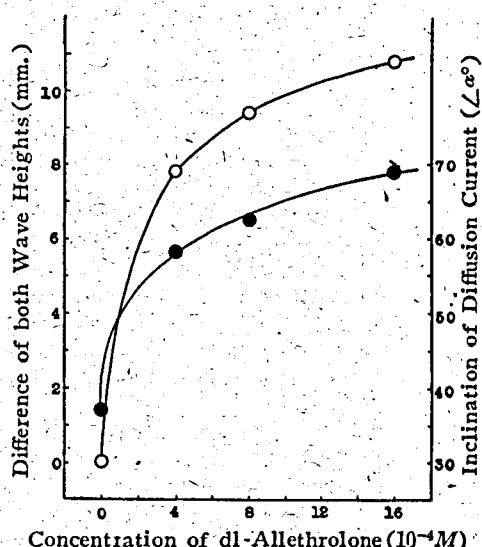


Fig. 11: Polarograms of related compounds of allethrin: I (pyruvaldehyde), II (allyl-acetone), III (dl-cis-chrysanthemum-monocarboxylic acid), IV (dl-trans-chrysanthemum-monocarboxylic acid). Each concentration is $16 \times 10^{-4} M$, and each polarogram begins at -0.09 v.

dl-allethrolone increased, the inclination of diffusion current ($\angle \alpha$) increased exponentially, and the double wave appeared. The first wave was due to α -dl-trans-allethrin, and the second wave to dl-allethrolone, and the two compounds were clearly distinguishable. In all cases, the reduction potential of α -dl-trans-allethrin remained the same as in the case α -dl-trans-allethrin alone was tested. Because the diffusion current of α -dl-trans-allethrin became steeper, the wave height calculated out by the above-mentioned construction method, became a little lower. Namely, as indicated by Fig. 12, the wave height



Concentration of dl-Allethrolone ($10^{-4} M$)

Fig. 12: Difference between wave height of α -dl-trans-allethrin alone and wave height when dl-allethrolone is added to it, and inclination of diffusion current of α -dl-trans-allethrin when dl-allethrolone is added to it: Concentration of each α -dl-trans-allethrin is $16 \times 10^{-4} M$. O, indicates difference of both wave heights (1mm. wave height = $3.09 \times 10^{-8} A.$); ●, indicates inclination of diffusion current.

decreased exponentially. In this graph, the left longitudinal axis shows the difference between the wave height of α -dl-trans-allethrin alone and the wave height when dl-allethrolone was added to it. In these cases, the error of determination of allethrin was from about -4.4% to about -7.5% .

b. Influence of dl-cis, trans-Chrysanthemum-monocarboxylate of 3-hydroxy-8-nonene-2.5-dione.

As indicated by Fig. 13, when dl-cis, trans-chrysanthemum-monocarboxylate of 3-hydroxy-8-nonene-2,5-dione (Sample 6) was added to α -dl-trans-allethrin, the diffusion current of α -dl-trans-allethrin became steeper. As the quantity of Sample 6 increased, the inclination of diffusion current ($\angle \alpha$) increased exponentially. On the other hand, however, ostensible diffusion current increased, too. If the quantity of Sample 6 shown in molar concentration was less than half of the quantity of α -dl-trans-allethrin, the wave height obtained was

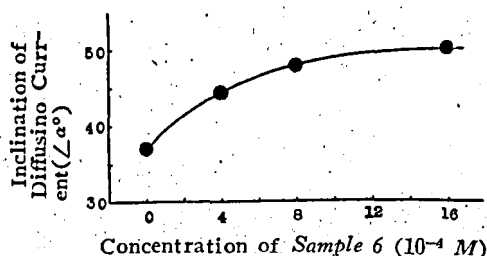


Fig. 13: Inclination of diffusion current of α -dl-trans-allethrin when crude matter of dl-cis,trans-chrysanthemum-monocboxylate of 3-hydroxy-8-nonene-2,5-dione (Sample 6) is added to it: Concentration of each α -dl-trans-allethrin is $16 \times 10^{-4} M$.

almost the same as the one when α -dl-trans-allethrin alone was tested. But when Sample 6 and α -dl-trans-allethrin were in the same molar, the wave height showed the increase of about 9%. In any of the above-mentioned cases, there was no change, as shown in the 5 line of Table 9, in the reduction potential of α -dl-trans-allethrin.

c. Influence of 3-hydroxy-8-nonene-2,5-dione.

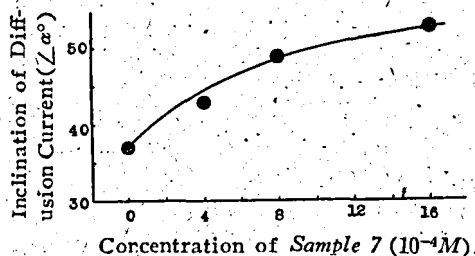


Fig. 14: Inclination of diffusion current of α -dl-trans-allethrin when crude matter of 3-hydroxy-8-nonene-2,5-dione (Sample 7) is added to it: Concentration of each α -dl-trans-allethrin is $16 \times 10^{-4} M$.

As indicated by Fig. 14, when 3-hydroxy-8-nonene-2,5-dione (Sample 7) was added to α -dl-trans-allethrin, the diffusion current of α -dl-trans-allethrin became steeper. As the quantity of Sample 7 increased, the inclination of diffusion current ($Z\alpha$) increased exponentially. On the other hand, however, ostensible diffusion current increased too. If the quantity of Sample 7 shown in molar concentration was less than half of the quantity of α -dl-trans-allethrin, the wave height obtained was almost the same as the one when α -dl-trans-allethrin alone was tested. But, when Sample 7 and

α -dl-trans-allethrin were in the same molar, the wave height showed the increase of about 5%. In any of the above-mentioned cases, there was no change, as shown in the 5 line of Table 9, in the reduction potential of α -dl-trans-allethrin.

The possibility that dl-allethrolone, Sample 6 or 7, exist in technical allethrin is great. As indicated in 3 of III, the result of the analysis of technical allethrin by the present authors showed that the diffusion current of technical allethrin was steep as compared with that of the pure α -dl-trans-allethrin, and technical allethrin with a low content of allethrin often showed the double wave on account of the unreacted allethrolone (e.g. No. 2 and 3 of Fig. 15). As a matter of fact, the authors separated dl-allethrolone from a certain technical allethrin by partition-chromatography. Judging from the process of the production, dl-allethrolone, Sample 6 or 7 cannot possibly exist so much that they are in the same molar as allethrin. The question is, therefore, the correction of errors caused by dl-allethrolone, which is now under study.*

3. Results of Determination of Allethrin in Technical Allethrins and Analytical Values of α -dl-trans-allethrin Added to the Technical Allethrins.

Technical allethrins produced by various makers both in Japan and the U. S. A. have been analysed by the method stated in I of III. As indicated by Fig. 15 and 16, the reduction waves showed such wave forms that the wave height could be measured by the above-mentioned method.

Next, the analyses were conducted after adding some quantity of pure α -dl-trans-allethrin to the technical allethrin. As the result, the quantity of added α -dl-trans-allethrin and the analytical values agreed fairly well, with some experimental errors in

* The polarographic determination of dl-allethrolone and the detailed study on the influence of dl-allethrolone upon the reduction wave of α -dl-trans-allethrin are now being continued, and will probably be published in the next report.

consideration.

As may be judged by the above-mentioned facts and the results of the study mentioned in 2 of III, if by the method of determination of allethrin introduced by the present authors, errors which may creep in are kept within the experimental errors with most of the samples. When unreacted allethrolone exist in comparatively large quantity in the sample, errors do not exceed -7.5%.

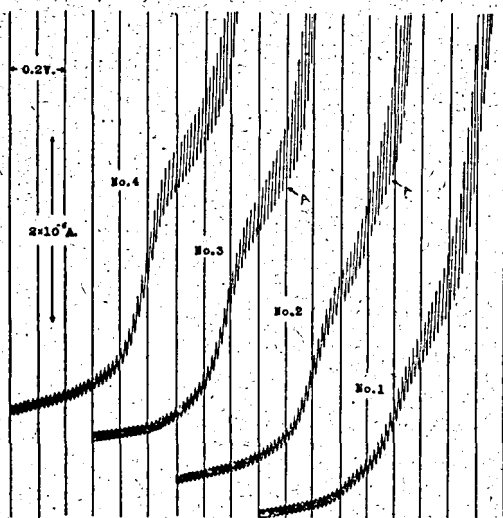


Fig. 15: Polarograms of some technical allethrins: No. 1 (allethrin content is 19%), No. 2 (allethrin content is 28%), No. 3 (allethrin content is 39%), No. 4 (allethrin content is 51%). Each number correspond to one of Table 10, and 6 mg. of sample is contained in each 10 cc. of electrolytic solution. A indicates the existence of unreacted dl-allethrolone. Each polarogram begins at -0.79 v.

EXPERIMENTAL

1. Apparatus.

A Heyrovsky-Shikata type polarograph (made by Yanagimoto Selsakusho Co.) was employed. The sensitivity of galvanometer employed was in all cases 3.09×10^{-8} A. per mm. per m. The capillary constants, measured at -1.0 v. in electrolytic solution mentioned in 1 of III, are as follows: $m=1.14$ mg. per sec., $t=4.42$ sec. per drop, $m^{2/3} t^{1/6}=1.398$.

2. Sample Used.

1) α -dl-trans-Chrysanthemum-monocarboxylate

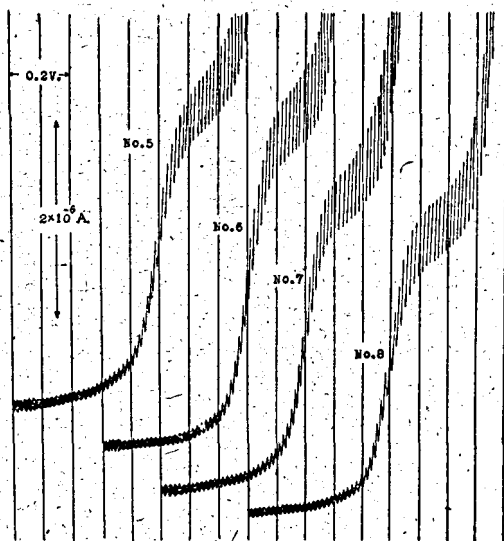


Fig. 16: Polarograms of some technical allethrins: No. 5 (allethrin content is 62%), No. 6 (allethrin content is 73%), No. 7 (allethrin content is 78%), No. 8 (allethrin content is 86%). Each number correspond to one of Table 10. Six mg. of sample is contained in 10 cc. of electrolytic solution for No. 5 and 6, and 4.8 mg. and 4.2 mg. for No. 7 and 8, respectively. Each polarogram begins at -0.79 v.

of dl-2-allyl-3-methyl-4-hydroxy-2-cyclopenten-1-one (α -dl-trans-allethrin).

This was obtained as crystals by cooling allethrin mixture at a low temperature and recrystallizing it from petroleum ether⁶, mp. 50.5~51°.

Anal. Calcd. $C_{19}H_{26}O_3$ C 75.46 H 8.67

Found 75.27 8.79

2) dl-cis, trans-Chrysanthemum-monocarboxylate of dl-2-allyl-3-methyl-4-hydroxy-2-cyclopenten-1-one (dl-cis, trans-allethrin).

This is a slightly yellowish matter obtained by purifying, by means of partition chromatography⁶, the oily ester mixture, which had been obtained by esterification of dl-allethrolone with dl-cis, trans-chrysanthemum-monocarboxylic chloride⁶, until the wave height did not rise any further (this took four times). Its wave height was, as mentioned in II almost the same as that of α -dl-trans-allethrin.

3) dl-cis-Chrysanthemum-monocarboxylate of dl-2-allyl-3-methyl-4-hydroxy-2-cyclopenten-1-

one (*dl-cis-allethrin*).

This is a slightly yellowish matter obtained by purifying, by means of partition chromatography⁽⁸⁾, the oily ester mixture, which had been obtained by esterification of *dl-allethrolone* with *dl cis-chrysanthemum-monocarboxylic chloride*⁽⁹⁾, until the wave height did not rise any further (this took four times). Its wave height was, as mentioned in II, almost the same as that of α -*dl-trans-allethrin*.

4) *dl-trans-Chrysanthemum-monocarboxylate of dl-2-allyl-3-methyl-4-hydroxy-2-cyclopenten-1-one (dl-trans-allethrin)*.

This is a slightly yellowish matter obtained by purifying, by means of partition chromatography⁽⁸⁾, the oily ester mixture, which had been obtained by esterification of *dl-allethrolone* with *dl-trans-chrysanthemum-monocarboxylic chloride*⁽⁹⁾, until the wave height did not rise any further (this took four times). Its wave height was, as mentioned in II, almost the same as that of α -*dl-trans-allethrin*.

5) *dl-2-Allyl-3-methyl-4-hydroxy-2-cyclopenten-1-one (dl-allethrolone)*.

This was obtained by cyclisation of 3-hydroxy-8-nonene-2,5-dione with sodium hydroxide and was isolated as described by F. B. LaForge⁽¹⁰⁾. bp. 117~118°/0.9 mm.

6) *dl-cis, trans-Chrysanthemum-monocarboxylate of 3-hydroxy-8-nonene-2, 5-dione (crude matter)*.

3-Hydroxy-8-nonene-2,5 dione was esterified with *dl-cis, trans-chrysanthemum-monocarboxylic acid chloride* in absolute benzene containing dry pyridine.

7) *3-Hydroxy-8-nonene-2, 5-dione (crude matter)*.

Following F. B. LaForge's procedure⁽¹⁰⁾, ethyl-3-oxo-6-heptenoate was hydrolysed with sodium hydroxide and the resulting solution of sodium salt was condensed with pyruvaldehyde at pH 8.0~8.5 and the product was isolated as described.

8) *Ethyl-3-oxo-6-heptenoate*.

This was obtained by the carbethoxylation of allyl acetone using the forced-condensation procedure with sodium methylate and ethyl

carbonate⁽¹¹⁾. bp. 111~117°/14 mm.

9) *5-Hexene-2-one (allyl acetone)*.

This was prepared through ethyl α -allyl-acetoacetate from ethyl monosodio-acetoacetate and allyl bromide by the ordinary procedure. bp. 127~132°.

10) *Pyruvaldehyde (methylglyoxal)*.

This was obtained by the selenium dioxide oxidation of acetone and distillation under reduced pressure⁽¹²⁾. Yellowish coloured, viscous liquid. Analysis by precipitation of 2,4-dinitrophenylosazone showed 81% purity.

11) *dl-cis, trans-Chrysanthemum-monocarboxylic acid*.

This mixture was obtained by the addition of ethyl diazoacetate to 2,5-dimethyl-2,4-hexadiene and saponification of the resulting product with alcoholic potash⁽¹³⁾. bp. 143°/12 mm.

12) *dl-cis-Chrysanthemum-monocarboxylic acid*.

This was isolated as crystals from the *cis, trans-acid* mixture dissolved in ethyl acetate by cooling at a low temperature and was recrystallized from the same solvent⁽¹³⁾. mp. 115~116°.

13) *dl-trans-Chrysanthemum-monocarboxylic acid*.

The filtrate from crystalline *cis-acid* was fractionated repeatedly under reduced pressure and the *trans-acid* crystallized out from a thick solution of ethyl acetate⁽¹³⁾. mp. 54°.

3. Influence of pH on Reduction Wave of α -*dl-trans-Allethrin*.

Buffer solutions of various pH's as shown in Table 2 were used, and the polarograms of α -*dl-trans-allethrin* were taken by the method described in I of III. The results are shown in Fig. 1~4.

4. Effect of Temperature on Reduction Wave of α -*dl-trans-Allethrin*.

The polarograms of α -*dl-trans-allethrin* were taken at various degrees of temperature by the method described in I of III, while the concentration and the composition of the electrolytic solution were kept constant. The wave heights and the inclinations of diffusion current ($\angle\alpha$) measured are shown in Table 3.

5. Relation between Concentration and Wave Height of α -*dl-trans-Allethrin*.

Table 2: Buffer Solution Used.

Classification		Actual pH Value* 25°C.
Clark and Lub's HCl-KCl	1.0	1.15
	2.0	2.15
Sørensen's HCl-Na-Citrate	2.97	2.96
	3.95	3.97
	4.96	5.01
Kolthoff's KH_2PO_4 -Borax	6.0(18°C.)	5.95
	7.0(18°C.)	6.90
	8.0(18°C.)	8.14
Sørensen's NaOH-Borax	9.18(26°C.)	9.19
	9.86(26°C.)	10.12
	10.91(26°C.)	10.86
	12.13(26°C.)	12.21

* This value was determined with an hydrogen electrode.

Table 3: Wave Heights and Inclinations of Diffusion Current of 16×10^{-4} M α -dl-trans-Allethrin at Different Temperatures.

Temperature °C.	Wave Height cm.	Inclination of Diffusion Current $\angle \alpha^\circ$
5.0 ± 0.2	5.80	14.5
10.2 ± 0.2	6.52	18.5
14.9 ± 0.2	7.30	25.5
21.0 ± 0.2	8.24	30.1
25.1 ± 0.2	8.90	34.6
29.0 ± 0.2	9.51	41.3

1 mm. wave height = 3.09×10^{-8} A.

Table 4: Wave Heights and Inclinations of Diffusion Current of α -dl-trans-Allethrin at Different Concentrations.

Concentration 10^{-4} M	Wave Height cm.		Inclination of Diffusion Current $\angle \alpha^\circ$
	Found	Calcd.	
2	1.22	1.13	38.0
4	2.16	2.25	37.0
8	4.61	4.50	33.3
12	6.77	6.76	25.8
16	8.88	9.01	18.5
20	11.38	11.26	15.8

1 mm. wave height = 3.09×10^{-8} A.
Temp.: $25 \pm 0.2^\circ\text{C}$.

The wave height and the inclination of

diffusion current ($\angle \alpha$) of α -dl-trans-allethrin at various concentration were determined by the method and under the conditions described in 1 of III. The results are shown in Table 4.

6. Change of Reduction Wave of α -dl-trans-Allethrin by Time.

The electrolytic solution of α -dl-trans-allethrin, which had the composition as shown in 1 of III, was left at $25 \pm 0.2^\circ\text{C}$. for a certain period of time. The polarograms were then taken, and the half-wave potentials, inclinations of the diffusion current ($\angle \alpha$) and wave heights were studied. The results are shown in Table 5. The values shown in the Table are the average figures taken by repeating each process twice.

Table 5: Wave Heights, Half-Wave Potentials and Inclinations of Diffusion Current of 16×10^{-4} M α -dl-trans-Allethrin of Which The Electrolytic Solution Is Left at $25 \pm 0.2^\circ\text{C}$. for a Certain Period of Time.

	Time		
	30 min.	6 hrs.	12 hrs.
Wave height cm.	9.06	9.10	9.04
Half-wave potential v.	ca.-1.27	ca.-1.27	ca.-1.27
Inclination of diffusion current $\angle \alpha^\circ$	37.0	37.1	37.1

7. Polarograms of Geometrical Isomers of Allethrin.

The polarograms were taken of dl-cis, trans-allethrin, dl-cis-allethrin, and dl-trans-allethrin by the method and under the conditions described in 1 of III. The results are shown in Fig. 7, and Table 6.

8. Influence of Ethyl-3-oxo-6-heptenonate, Pyruvaldehyde, and dl-cis, trans-Chrysanthemum-monocarboxylic Acid on Reduction Wave of α -dl-trans-Allethrin.

Electrolytic solutions were prepared, each one of which contained α -dl-trans-allethrin and either one of ethyl-3-oxo-6-heptenonate, pyruvaldehyde and dl-cis, trans-chrysanthemum-monocarboxylic acid in the same

Table 6: Wave Heights of dl-cis,trans-, dl-cis-, and dl-trans-Allethrin at Different Concentrations.

Concentration $10^{-4} M$	Wave height, found cm.		
	dl-cis, trans-	dl-cis-	dl-trans-
2	1.22	1.23	1.06
4	2.10	2.15	2.14
8	4.51	4.30	4.53
12	6.53	6.75	6.56
16	8.89	8.76	9.00

1 mm. wave height = 3.09×10^{-8} A.Temp. : $25 \pm 0.2^\circ C$.

molar. The quantitative analyses of α -dl-trans-allethrin in these solutions gave the results as shown in Table 7. The values shown in the Table are the average figures taken by repeating each process twice. These experiments were performed by the method and under the conditions described in 1 of III.

9. Influence of dl-Allethrolone on Reduction Wave of α -dl-trans-Allethrin.

As described in 1 of III, electrolytic solutions were prepared, which contained α -dl-trans-allethrin and dl-allethrolone and the related compounds of allethrin in various proportions, and α -dl-allethrin was analysed quantitatively. The results are shown in Fig. 9,

and Table 8. The values shown are the average figures taken by repeating each process twice.

10. Influence of dl-cis,trans-Chrysanthemum-monocarboxylate of 3-Hydroxy-8-nonene-2,5-dione and 3-Hydroxy-8-nonene-2,5-dione.

As described in 1 of III, electrolytic solutions were prepared, which contained α -dl-trans-allethrin, dl-cis,trans-chrysanthemum-monocarboxylate of 3-hydroxy-8-nonene-2,5-dione and 3-hydroxy-8-nonene-2,5-dione in various proportions, and α -dl-trans-allethrin was analysed quantitatively. The results are shown in Table 9. The values shown are the average figures, taken by repeating each process twice.

11. Results of Determination of Allethrin in Technical Allethrins and Analytical Values of α -dl-trans-allethrin added to the Technical Allethrins.

Technical allethrins produced by various makers both in Japan and the U. S. A. have been analysed by the method stated in 1 of III, and the polarograms and the results are shown in Fig. 15 and 16, and Table 10, respectively. In the polarograms of Sample No. 3~No. 8, where allethrin content exceeded 39%, the wave height could be measured easily. When

Table 7: Determinations of α -dl-trans-Allethrin in Synthetic Samples. 1.

		No. 1	No. 2	No. 3	No. 4
α -dl-trans-Allethrin	$10^{-4} M$	1.60	1.60	1.60	1.60
I *	$10^{-4} M$		1.60		
II *	$10^{-4} M$			1.60	
III *	$10^{-4} M$				1.60
Half-wave potential of α -dl-trans-Allethrin, found	v.	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.27
Inclination of diffusion current, found	$\angle \alpha^\circ$	37.0	35.5	40.0	44.8
Wave height, found	cm.	9.01	9.01	8.95	9.00
Concentration of α -dl-trans-allethrin, found	$10^{-4} M$	1.60	1.60	1.59	1.60
Error	%		0	-0.6	0

* I: Ethyl-3-oxo-6-heptenoate.

II: Pyruvaldehyde.

III: dl-cis,trans-Chrysanthemum-monocarboxylic acid.

Table 8: Determinations of α -dl-trans-Allethrin in Synthetic Samples. 2.

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
α -dl-trans-Allethrin 10^{-4} M	1.60	1.60	1.60	1.60	0.80	0.80	1.60
dl-Allethrolone 10^{-4} M		1.60	0.80	0.49	0.80	0.80	0.80
I *						0.80	0.80
II *							0.60
III *							0.40
IV *							0.40
V *							0.40
Half-wave potential of α -dl-trans-allethrin, found v.	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.27
Inclination of diffusion current, found $\angle \alpha^\circ$	37.0	69.0	62.7	58.3	58.6	49.0	66.5
Wave height, found cm.	9.01	8.32	8.46	8.62	4.28	4.28	8.57
Concentration of α -dl-trans-allethrin, found 10^{-4} M	1.60	1.48	1.50	1.53	0.76	0.76	1.52
Error %		-7.5	-6.2	-4.4	-5.0	-5.0	-5.0

* I: dl-cis,trans-Chrysanthemum-monocarboxylate of 3-hydroxy-8-nonene-2,5-dione (crude matter).

II: 3-Hydroxy-8-nonene-2,5-dione(crude matter).

III: Ethyl-3-oxo-heptenoate.

IV: Pyruvaldehyde.

V: dl-cis,trans-Chrysanthemum-monocarboxylic acid.

The concentrations of I and II are shown by assuming these as pure matter.

Table 9: Determinations of α -dl-trans-Allethrin in Synthetic Samples. 3.

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
α -dl-trans-Allethrin 10^{-4} M	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
I *		1.60	0.80	0.80	0.40	0.40			
II *				0.80		0.40	1.60	0.80	0.40
Half-wave potential of α -dl-trans-allethrin, found v.	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.27	ca. -1.72	ca. -1.27	ca. -1.27	ca. -1.27
Inclination of diffusion current, found $\angle \alpha^\circ$	37.0	50.5	48.0	56.5	44.5	45.0	53.0	49.0	43.3
Wave height, found cm.	9.01	9.84	9.06	9.03	9.01	9.16	9.38	8.84	8.85
Concentration of α -dl-trans-allethrin, found 10^{-4} M	1.60	1.75	1.61	1.62	1.60	1.63	1.67	1.57	1.57
Error %		+9.4	+0.6	+1.3	0	+1.9	+4.7	-1.9	-1.9

* I: dl-cis,trans-Chrysanthemum-monocarboxylate of 3-hydroxy-8-nonene-2,5-dione (crude matter).

II: 3-Hydroxy-8-nonene-2,5-dione(crude matter).

The concentrations of I and II are shown by assuming these as pure matter.

the allethrin content was low as in Sample No.1, however, the measuring became slightly difficult. In this case, therefore, the analysis was conducted by the method of C-2 in I of III. The analysis was conducted after adding

Table 10: Determinations of Allethrin in Technical Allethrins and Analytical Values of α -dl-trans-Allethrin Added to Those Technical Allethrins.

		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Technical allethrin	Technical allethrin mg.	6.0	6.0	6.0	6.0	6.0	6.0	4.8	4.2
	α -dl-trans-allethrin, added mg.	1.22							
	Wave height, found cm.	4.34	3.09	4.31	5.67	6.96	8.10	6.99	6.77
	Concentration of allethrin, found $10^{-4} M$	0.771	0.549	0.769	1.007	1.236	1.439	1.242	1.202
	Allethrin, found (I) mg.	1.11	1.66	2.32	3.04	3.73	4.35	3.75	3.63
	Allethrin, found % (Allethrin, determined by each maker %)	19	28	39	51	62 (75)	73 (75)	78 (75)	86 (90)
α -dl-trans-Allethrin added to technical allethrin	Technical allethrin mg.	6.0	6.0	6.0	6.0	6.0	6.0	4.8	4.2
	α -dl-trans-allethrin, added (II) mg.	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
	Wave height, found cm.	3.13	4.16	5.34	6.78	8.01	9.19	8.11	7.85
	Concentration of allethrin, found $10^{-4} M$	0.556	0.739	0.948	1.202	1.423	1.632	1.440	1.394
	Allethrin, found (III) mg.	1.68	2.23	2.86	3.63	4.30	4.93	4.35	4.21
	α -dl-trans-Allethrin, found (III-I; IV) mg.	0.57	0.57	0.54	0.59	0.57	0.58	0.60	0.58
	Difference between II and IV (V) mg.	-0.03	-0.03	-0.06	-0.01	-0.03	-0.02	0	-0.02
	Error (V/II) %	-5.0	-5.0	-10	-1.7	-5.0	-3.3	0	-3.3

some quantity of pure α -dl-trans-allethrin to the technical allethrins of No. 1~No. 8, which had been analysed as mentioned above. The results are as in Table 10.

CONCLUSION

1. When the isomers of allethrin were reduced at dropping mercury electrode in the electrolytic solution of ethyl alcohol (50%), $M/5$ $(CH_3)_4NBr$ solution (10%), and Sørensen's buffer solution of pH 2.97 (40%), the typical reduction waves were obtained.
2. The reduction waves of the geometrical isomers of allethrin were identical, and the half-wave potentials of them were all about -1.27 v. at $25 \pm 0.2^\circ C$. in the solution.
3. The wave heights of each geometrical isomer of allethrin were proportional to the concentrations.
4. When at the different pH values α -dl-trans-allethrin was reduced, the reduction waves of various different types were obtained.
5. As the temperature increased, the half-wave potential of α -dl-trans-allethrin shifted to the negative potential, and the wave height

increased proportionally.

6. The determination of allethrin by polarographic method was devised after the above-mentioned investigation and the study on the accuracy of this method with various synthetic and technical samples were performed. This method gave the reliable and satisfactory results; errors which might creep in were kept within the experimental errors with most of the samples. However, when unreacted allethrolone existed in comparatively large quantity in the sample, some degrees of errors occurred.

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抄 録

Cumarone resin 添加による DDT-Residue の効力の増大 N. van Tiel: Bull. Ent. Res., 43, 413 (1952)

DDT-residue の殺虫力は撒布後そこにできる結晶の particle size と密接な関係があり、それが小さくなる程効力は増大する。この particle size は用いた solvent の揮発性と関係があり、それが早い程小さいことが知られているが、このような高揮発性の solvent の多くは有毒ガスを生成し、ときに爆発性を有する難点がある。著者は DDT-residue の効果を高めるための方法を研究し、生成される残渣結晶粒度と効力との間に明瞭な関係のあることを実験的に再確認した。試験昆虫としてはイエバイを用いた。xylene のような揮発性の早い solvent を用いると DDT 残渣の結晶は kerosene を solvent に用いたときより微細となり殺虫力も増大した。しかし kerosene を

用いてもこれに cumarone resin の少量を添加すると残渣の結晶粒度が小さくなり、その効力も著しく増大することが発見された。この協力的な効果は resin の濃度が DDT の 10% のとき最大となりそれ以上多く添加すると resin のために DDT 結晶が覆われて効力が減少傾向をとる。resin と DDT の比が1:2になると resin の添加は拮抗的效果をもたらす、これを添加しない場合よりかえつて効果が減少する。

(1% DDT+0.1% resin) の残渣の効力は 5% DDT の残渣よりも有効で、その優位は 69 日間保持された。しかし (3% DDT+0.3% resin) の残渣は 5% DDT に比し更に永続的に高い効力を示した。この結果はガラス板の上で得たものであるが、実際に応用する場合の他の物質表面、たとえば、鉄、塗装しない木、紙、綿布、モルタル等の表面でもこの傾向が認められた。(河野達郎)

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