solution. Titrate free iodine with 0.2N sodium thiosulfate solution.

Calculation :

$$\frac{\text{ml of } 0.2N\ Na_2S_2O_3 \times 0.003166}{\text{weight of sample}} \times 100 = \text{methylbromide } \%$$

$$\frac{\{\text{ml of } 0.1N\ AgNO_3 - (CH_3Br\,(g) \div 0.009495)\} \times 0.003546 \times 1.5463}{\text{weight of sample}} \times 100 = \text{chlorpicrin}\%$$

Polarographic Determination of Allethrolone. (Studies on Determination of Pyrethroids. IJ.) Toshihiko Oiwa, Yuzo Inouye, Jiyouzo Ueda, and Minoru Ohno (Takei Laboratory, Institute for Chemical Research, Kyoto University) Received May 1, 1953. *Botyu-Kagaku*, 18, 60 (1953).

14. アレスロロンのポーラログラフ法による定量*（ピレトリン類縁物質の定量に関する研究. 第2報）

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28. 5. 1 受理

dl-Allethrolone は式 I の様な構造で，最近問題になつている合成殺虫剤 allethrin の中間原料である。Allethrin の合成過程から考えて，dl-allethrolone の純度を正確に知ることは非常に必要なことであるが，現在迄に吉田**が化学的の方法を発表した以外には，定量法が知られていない。著者等は第1報[1]の allethrin の定量法にならつて，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，こゝに発表して大方識者の批判を仰ぐ次第である。

定量の標準として用いた dl-allethrolone は，著者等[2]が先に合成した粗品を分別クロマトグラフ法によって充分に精製したもので，ethyl alcohol を溶媒として測定した紫外部吸収スペクトルの極大の波長は 2295 Å，又その波長に於ける分子吸光系数は 11049 である。

dl-Allethrolone を水銀滴下電極で，ethyl alcohol (50%), $M/5$ tetramethyl ammonium bromide 溶液(10%)，緩衝液 (40%) なる組成の電解液中で還元した処，典型的な還元波が得られた。この組成で，Table 1 に示す pH 値の異る12種の緩衝液を用いポーラログラムを撮つて，Fig. 1~3 に示す種々の形の還元波を得た。これらの還元波を比較検討して，定量に最適の緩衝液の pH は 2.0 の附近であることを知つた。pH 2.00 の Sörensen の緩衝液を用いた場合，電解液の pH は 2.56 であり，半波電位 (N-甘汞電極規準) は −1.32 v. である。

次に，電解液の pH 2.56，濃度 16×10^{-4} M で，dl-allethrolone の還元波に及す温度の影響を検討した。その結果は，温度の上昇と共に半波電位は僅かづゝ負に移行し，又波高は Fig. 4 に示す様に直線的に増加し，その関係は式1で示された。この関係式から定量操作のし易い 25° 附近で温度の変化に基く誤差を ±1% 以内に留めるには，還元温度を ±0.6° 内に保つ必要があることが解る。

更に，電解液の pH 2.56，上述の電解液組成で，還元温度を 25±0.2° に保つて，種々の濃度の dl-allethrolone のポーラログラムを撮り，波高を測定した処，濃度と波高の関係は Fig. 5 及び式2に示す様に座標軸の原点を通る直線で表わされた。従つてこの関係式を用いて逆に波高から電解液中の dl-allethrolone の濃度を求めることができる。

以上の諸結果と第1報の allethrin の定量法とを考慮して，dl-allethrolone の定量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. を栓附試験管に秤取し，これに ethyl alcohol 4 cc. と $M/5$ tetramethyl ammonium bromide 液 1 cc. を加え，次に pH 約 2.0 の Sörensen の緩衝液 4 cc. を加える。振盪後，陽極の水銀を入れ，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±0.5° でポーラログラムを撮る。尚 dl-allethrolone の含量が 20% 以下の工業製品になると，混在する不純物の為に一般に波形が不明瞭となり，作図が困難となる。従つてこの様な試料では，電解液中に特に一定量の標準 dl-allethrolone を加えて，明瞭な形の還元波を得る様にする。かくして得たポーラログラムは Fig. 6 に示す作図法に依つて波高を測定し，標準 dl-allethrolone の濃度と波高の関係式から dl-allethrolone の含量を求める。

この方法の精度の検討を次の2つの方面から行つた。

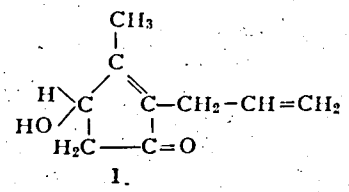
* 日本農芸化学会大会（1953年4月7日）で発表。

** 吉田英寛：第6回日本薬学大会（1953年4月6日）

即ち先ず第1に allethrolone の工業製品中に夾雑してくる可能性のある中間原料の影響の検討を行つたが，かゝる中間原料として考えられる主なものは，3-hydroxy-8-nonene-2,5-dione, ethyl-3-oxo-6-heptenoate, allyl acetone 及び pyruvaldehyde である。第1報で報告した様に −0.1 v. から −1.6 v. の間では，これらの化合物自身は何れも還元波を示さないが，dl-allethrolone の還元波に影響を与える懸念はある。そこで dl-allethrolone とこれらの化合物 (3-hydroxy-8-nonene-2,5-dione は粗品) とを種々の割合に調合した合成試料をつくり，その中の dl-allethrolone を定量した処，Table 5 及び 6 に示す様に何れも影響のないことを知つた。第2には，種々の allethrolone 工業製品を実際に定量してみたが，何れも作図可能の波形を示した。今その一例を示すと Fig. 7 及び Table 7 の様である。更にこれらの製品に一定量の標準 dl-allethrolone を特に加えたものを定量した処，添加値と定量値とは Table 7 の下段に示す様によく一致した。以上の事からこの定量法で，工業製品を定量する際生ずる誤差は先ず実験誤差内と考えてよい。

本研究は武居三吉教授の御指導で行つた。こゝに深謝する。又研究費の一部は文部省科学試験研究費に仰いだ。

Allethrolone shown in I is an intermediate material of allethrin---a much-talked-about synthetic insecticide. As is known, in producing allethrin the exact knowledge of purity of allethrolone is necessary, for it serves as a time-saving and quality-improving factor. But the adequate method of the determination has not been known yet. The authors have experimented on the determination of allethrolone by polarographic method as they[1] did in estimating allethrin. As the result, they have arrived at a comparatively reliable and satisfactory method such as follows.



1.

I. PREPARATION OF STANDARD dl-ALLETHROLONE

The dl-allethrolone used as the standard of determination has been prepared in the following manner. The crude dl-allethrolone, synthesized according to the procedure the authors[2] have reported earlier, was thoroughly purified by column partition chromatography until at last the wave height of the polarogram of the dl-allethrolone became constant. The wave length of maximum of ultraviolet absorption spectrum of this substance in the ethyl alcohol solution is 2295 Å, and the molecular extinction coefficient in this case is 11040.

II. POLAROGRAM OF dl-ALLETHROLONE

1. Preparation of Electrolytic Solution.

The composition of the electrolytic solution was the same as the case given in the first report[1] and is as follows:

Ethyl alcohol (50%), and $M/5$ $(CH_3)_4NBr$ solution (10%), and buffer solution (40%). As stated in later paragraphs, the typical reduction wave can be obtained in this composition of the electrolytic 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 dl-allethrolone were taken, with the aid of various buffer solutions, by the method and under the conditions described in 1 of III. The result is shown in Fig. 1~3. The values of pH in the figures are of the electrolytic solution.

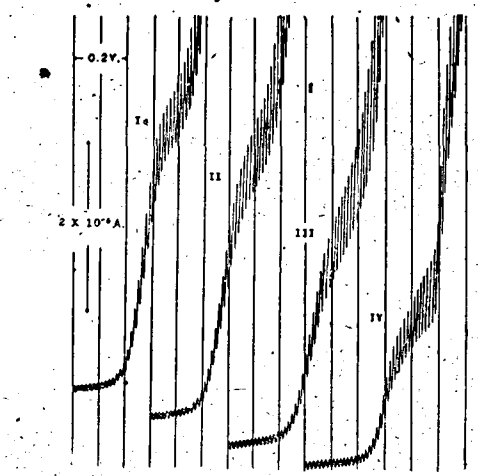


Fig. 1—Polarograms of 2×10^{-3} M dl-allethrolone reduced at different pH values: I(pH=1.57) begins at −0.90 v. II (pH=2.56) begins at −1.00 v. III (pH=3.70) begins at −1.10 v. IV (pH=4.79) begins at −1.20 v.

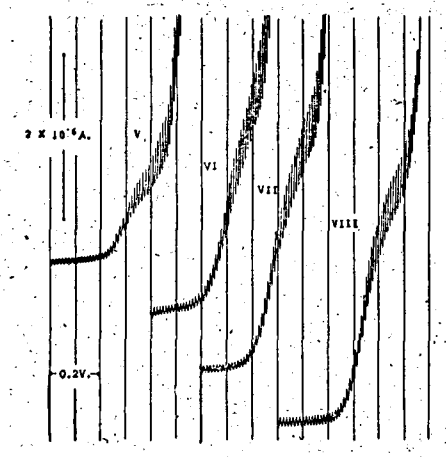


Fig. 2—Polarograms of $2\times10^{-3}M$ dl-allethrolone reduced at different pH values: V (pH=5.77) begins at−1.30 v. VI (pH=6.85) begins at−1.50v. VII(pH=7.87)begins at−1.50 v. VIII (pH=9.56) begins at−1.50 v.

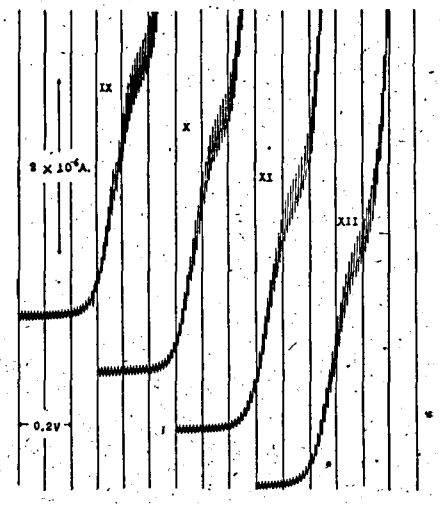


Fig. 3—Polarograms of $2\times10^{-3}M$ dl-allethrolone reduced at different pH values: IX(pH=10.73)begins at−1.50 v. X(pH=11.34)begins at−1.50 v. XI(pH=12.00) begins at−1.50 v. XII(pH=13.07) begins at−1.57 v.

As evident from the figures, the wave forms of I (1.57), II (2.56), III (3.76), IV (4.79), and V (5.77) are all different, and as the value of pH increases, the reduction potential shows a gradual but considerable shifting to the negative, while the wave height largely decreases. Half-wave potential in II is −1.32 v. (*vs.* N. C. E.).

In VI (6.85) the reduction potential moves still more greatly to the negative. Contrary to the case observed in the group I~V, the wave forms of VI (6.85), VII (7.87), VIII (9.56), IX (10.73), X (11.34), XI (12.00), and XII (13.07) resembled each other, and the reduction potential shifts gradually and only slightly to the negative as the value of pH increases. The wave heights of the polarograms of this group are almost identical except that of VI and VII which are lower than those of others.

The authors, after carefully comparing those polarograms, and considering the easiness or difficulties in measuring wave height in respective cases, decided that the value of pH of the buffer solution used suitable for the analysis is about 2.0.

3. Effect of Temperature on Reduction Wave.

The polarograms of dl-allethrolone 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. As the temperature increased, the half-wave potential shifted slightly to the negative potential. The wave height increased linearly in proportion to the increase of temperature, as shown in Fig. 4.

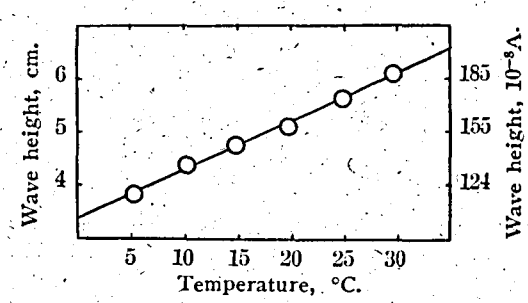


Fig. 4—Wave heights of $16\times10^{-4}M$ dl-allethrolone at different temperatures.

The theoretical equation of the curve is as below:

$$id = 0.091\ T + 3.38 \cdots\cdots\cdots\cdots (1)$$

In this equation id shows the wave height in centimeter and T signifies the temperature in Centigrade. Under these circumstances, therefore, the positive temperature coefficients of the wave height varied between about 2.4% at 5°C. and about 1.5% at 30 C.

Consequently, from the analytical viewpoint, it is evident that the temperature should be

controlled at least to the range of ±0.6°C., or better, in order to keep errors due to the temperature change within ± 1%, when the temperature is about 25°C., at which the analytical procedure is comparatively simple.

4. Relation between Concentration and Wave Height.

By the method and under the conditions described in 1 of III, the relation between the concentration and the wave height of dl-allethrolone was studied, and the result obtained is shown in Fig. 5.

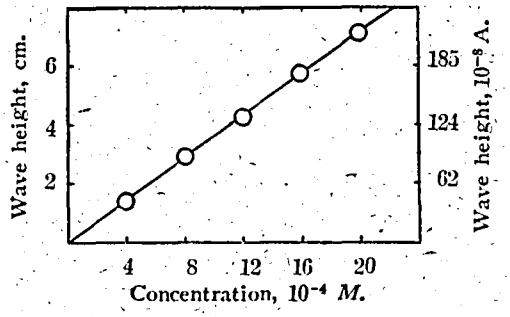


Fig. 5—Wave heights of dl-allethrolone at different concentrations.

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

$$id = 0.355\ C - 0.004 \quad \cdots\cdots\cdots\cdots (2)$$

where, id is the wave height in centimeter, and C is the concentration shown in unit of 10^{-3} *M*. Therefore, the wave height is proportional to the concentration, and the calculated values and experimental values are almost the same, with possible experimental errors considered. Conversely, therefore, the concentration of dl-allethrolone in the electrolytic solution can be calculated precisely from the wave height.

The change by time of the reduction wave under the conditions described in 1 of III was studied. Neither the wave form nor the wave height showed any change after 2 hours at 25 ± 0.2° C.

III QUANTITATIVE DETERMINATION OF dl-ALLETHROLONE

The following is the method of determination of dl-allethrolone deviced after the above mentioned fundamental investigations, and the study of the accuracy of this method with various samples.

1. Method of Analysis.

a. Electrolytic Cell.

The electrolytic cell is of the same type as used by M. Nakazima et al.[3], in quantitative analysis of BHC. This cell can easily keep the temperature of electrolytic solution constant.

b. Standard dl-Allethrolone.

The crude matter synthesized by the usual method[2,4,5] is further purified by distillation or by the column partition chromatography (as shown in the Experimental Part) until at last the wave height of the polarogram or the molecular extinction coefficient becomes constant.

c. 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 it is redistilled.

2) M/5 $(CH_3)_4NBr$ solution: Tetramethylammonium bromide is purified by recrystallization from alcohol, and dissolved into distilled water.

3) Buffer solution: Sörensen's sodium citrate-hydrochloric acid buffer solution of pH about 2.0.

4) Hydrogen: Oxygen is completely removed beforehand by passing it through at least five pyrogarol washing bottels (10 g. of pyrogarol 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.

d. Procedure.

1) Sample with dl-Allethrolone Content above about 20 %.

About 60 mg. of sample (weight must be measured 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 $M/5$ $(CH_3)_4NBr$ solution. To this solution, 4 cc. of buffer solution is added and shaken. This is poured into the electrolytic cell which contains anode mercury, whose temperature is kept at $25 \pm 0.5°$ C. When the procedure is over, dissolved oxygen is removed from the solution at $25 \pm 0.5°$ 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 $25 \pm 0.5°$ C.

2) Sample with dl-Allethrolone Content below about 20%.

As stated later, generally the wave form is obscure and the construction becomes difficult, when the dl-allethrolone content in technical product is below 20%. If, therefore, the experimenter finds out by the above-mentioned method that the sample belongs to this category, it is advisable for him to add a certain amount of standard dl-allethrolone 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 2×10^{-3} M standard dl-allethrolone ethyl alcohol solution, and 1 cc. of $M/5$ $(CH_3)_4NBr$ 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 dl-allethrolone is calculated from Eq. 2 prepared of the standard dl-allethrolone through the similar process.

e. Method of Measuring the Wave Height.

The method of construction is the same as in the case of allethrin.[1] As indicated by Fig. 6, a slope line is drawn through the center of oscillation. A straight tangent line (AB) is drawn to the diffusion current part of the slope line, and another straight tangent line (CD) is drawn at the bending at the foot in parallel with the line (AB). Then, a tangent 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 (∠FGA and ∠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.

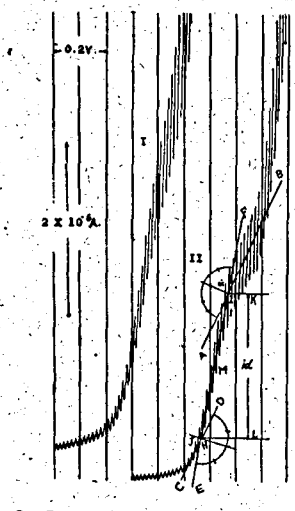


Fig. 6—I : Polarogram of mixture (No. 7 of Table 6) of 16×10^{-4} M dl-allethrolone and 16×10^{-4} M 3-hydroxy-8-nonene-2,5-dione (crude matter). This begins at −1.00 v.

—I : Method of measuring wave height.

2. Influence of Related Compounds on Reduction Wave of dl-Allethrolone.

The result of the study on the influences of the intermediate substances (allyl acetone, pyruvaldehyde, ethyl-3-oxo-6-heptenoate, 3-hydroxy-8-nonene-2, 5-dione), which might contaminate the technical allethrolone in the process of its production, is as follows. As stated in the first paper,[1] 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 dl-allethrolone. To study this, many samples of dl-allethrolone added with those

substances in various proportions were prepared, and the analyses of dl-allethrolone in each samples were made. Allyl acetone, pyruvaldehyde, and ethyl-3-oxo-6-heptenoate have no influence at all. As indicated by Fig. 6, when 3-hydroxy-8-nonene-2, 5-dione(crude matter) was added to dl-allethrolone, the diffusion current of dl-allethrolone became steeper. However, the errors arising from such change in the wave form can be avoided by the application of the construction method described in 1-e of III.

3. Results of Determination of dl-Allethrolone in Technical Products and Analytical Values of dl-Allethrolone Added to Technical Products.

Technical products produced by various makers have been analysed by the method stated in 1 of III. As indicated by Fig. 7, the reduction waves showed such wave forms that the wave height could be measured by the above-mentioned method.

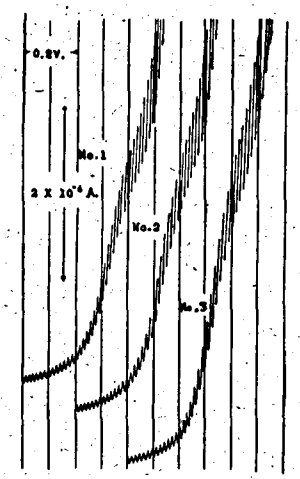


Fig. 7—Polarograms of some technical products: No. 1 (dl-allerhrolone content is 26%). No. 2 (dl-allethrolone content is 29%). No. 3 (dl-allethrolone content is 40%). Each number corresponds to one of Table 7, and 6.00 mg. of technical product is contained in each 10 cc. of electrolytic solution. Each polarogram begins at −1.00 v.

Next, the analyses were conducted after adding some quantity of standard dl-allethrolone to the technical products. As the result, the quantity of added dl-allethrolone and the analytical values agreed fairly well, with some experimental errors in consideration.

As may be judged by the above-mentioned facts and the results of the study mentioned in 2 of III, by the method of determination of dl-allethrolone introduced by the present authors, errors which may creep in are kept within the experimental errors with most of the samples.

EXPERIMENTAL

1. Apparatus.

A Heyrovskȳ-Shikata type polarograph (made by Yanagimto Seisakusho 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 the electrolytic solution mentioned in 1 of III were as follows:

$m = 0.697$ mg/sec, $t = 4.43$sec/drop., $m^{2/3}t^{1/6} = 1.002$

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

2. Samples Used.

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

The crude dl-allethrolone (bp. 110～118/0.9 mm.) was obtained by cyclization of 3-hydroxy-8-nonene-2,5-dione with sodium hydroxide and was isolated as described in earlier report[2]. This matter was purified by column partition chromatography* in nitrogen gas.

Preparation of the partition chromatographic column: To 100 g. of silicic acid (the size** of the particles was about 20～30 mμ) in a large mixing vessel, 10 g. of nitromethane was added in successive 2 g. (or thereabout) portions and mixed thoroughly after each addition. Then about 200 g. of the mixture of *n*-hexane and ether(1:1) was added in successive 20 g. (or thereabout) portions, and mixed thoroughly until it became a slurry. The resultant slurry was poured into an absorption tube (pyrex pipe,

* About the apparatus and the procedure of column partition chromatography, refer to: O. T. Aepli, P. A. Munter, and J. F. Gall: Anal. Chem., **20**, 610 (1948).

** This was measured with electron microscope by Mr. M. Arakawa of this Institute. absorption tube (pyrex pipe, 70 cm.

70 cm long × 2.4 cm. inside) and pressure (nitrogen gas) was applied on it. When there was sufficient space in the tube, the rest of the slurry was poured in, and pressure was applied again on it. When the gel became so firm that it retained its shape on tipping, the pressure was released.

Procedure of separation: The 5 g. of crude dl-allethrolone was dissolved in the 10 cc. mixture (mobile solvent) of *n*-hexane and ether (1 : 1). This solution was transferred to the absorption column, carefully so that the top of the gel was not disturbed. The pressure line was connected to the column and sufficient pressure was applied to cause the solvent to percolate through the column at the rate of about 5 cc. per minute. The instant all the solution had sunk into the gel, the pressure was released. Then the tube was filled with the mobile solvent and the pressure was applied again. After a certain volume of percolated solution had passed through the column, fractionation was begun, 30 cc. of the solution being collected in each fraction, and the solvent was removed at the diminished pressure in the warm bath, of which the temperature was at 40～50° C. The fractions were collected until no significant amount of material came through the column, and seven percolate fractions [No. 1 (0. 21 g.), No. 2 (0. 91 g.), No. 3 (1. 21 g.), No. 4 (1. 11 g.), No. 5 (0. 98 g.), No. 6 (0. 11 g.), No. 7 (trace)] were obtained. The matters of fractions No. 4 and 5 (judging from their wave heights the content of dl-allethrolone in these two fractions was supposed to be the greatest in comparison with that of others.) were combined and were refractionated in a fresh column of the same size. The middle fractions (likewise, the content of dl-allethrolone in these was the greatest.) were collected and purified by the same procedure until at last the wave height of the polarogram became constant, and 1. 01 g. of substance was obtained. The wave length of maximum of ultraviolet absorption spectrum of this matter in the ethyl alcohol solution was 2295 Å, and the molecular extinction coefficient in this case was 11049. These optical data were measured with Beckman's D. U. Spectrophotometer.

2) 3-Hydroxy-8-nonene-2,5-dione(crude matter). Following F. B. LaForge's procedure[4], 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. 2 and the product was isolated as described.

3) Ethyl-3-oxo-6-heptenoate. bp. 107～111°/14mm.
5-Hexene-2-one-(allyl acetone). bp. 128°.
Pyruvaldehyde (methyl glyoxal). bp. 60～70°/60 mm.

The substances used in the former experiment[4] were used after distillation.

3. Influence of pH on Reduction Wave of dl-Allethrolone.

Buffer solutions of various pH's as shown in Table 1 were used, and the polarograms of dl-allethrolone were taken by the method described in 1 of III. The measured values of pH's of these electrolytic solutions are shown in the third column of Table 1, and the polarograms are shown in Fig. 1～3.

Table 1
Buffer Solutions Used and pH Values of Electrolytic Solution

Buffer solution used: Classification	Actual pH value*, 25 ± 0. 2°C.	pH Value* of electrolytic solution, 25 ± 0. 2°C.
Sörensen's HCl-Na-citrate 1. 04	1. 04	1. 57
Sörensen's HCl-Na-citrate 2. 27	2. 00	2. 56
Sörensen's HCl-Na-citrate 2. 97	2. 96	3. 70
Sörensen's HCl-Na-citrate 3. 95	3. 97	4. 79
Sörensen's HCl-Na-citrate 4. 96	5. 01	5. 77
Kolthoff's KH_2PO_4-borax 6. 0 (18°C.)	5. 91	6. 85
Kolthoff's KH_2PO_4-borax 7. 0 (18°C.)	6. 87	7. 87
Kolthoff's KH_2PO_4-borax 8. 0 (18°C.)	8. 10	9. 56
Sörensen's NaOH-borax 9. 18(26°C.)	9. 19	10. 73
Sörensen's NaOH-borax 9. 86(26°C.)	9. 88	11. 34
Sörensen's NaOH-borax 10. 91(26°C.)	10. 93	12. 09
Sörensen's NaOH-borax 12. 13(26°C.)	12. 16	13. 07

* These values were determined with a hydrogen electrode.

4. Effect of Temperature on Reduction Wave of dl-Allethrolone.

The polarograms of dl-allethrolone were taken at various degrees of temperature by the method described in 1 of III. while the concentration and the composition of the electrolytic solution were kept constant. The half-wave potentials and the wave heights are shown in Table 2.

Table 2

Wave Heights of 16×10^{-4} *M* dl-Allethrolone at Different Temperatures

Temperature	Wave height		Half-wave potential
°C.	cm.	10^{-8} A.	v.
5.2 ± 0.2	3.82	118.04	−1.30
10.2 ± 0.2	4.38	135.34	−1.31
14.8 ± 0.2	4.72	145.85	−1.31
19.7 ± 0.2	5.12	158.21	−1.32
24.7 ± 0.2	5.65	174.59	−1.32
29.7 ± 0.2	6.10	188.49	−1.32

5. Relation between Concentration and Wave Height of dl-Allethrolone.

The wave heights of dl-allethrolone at various concentrations were determinad by the method and under the conditions described in 1 of III. The results are shown in Table 3.

Table 3

Wave Heights of dl-Allethrolone at Different Concentrations

Concentration	Wave height			
	Found		Calcd.	
10^{-4} *M*.	cm.	10^{-8}A.	cm.	10^{-8}A.
4	1.40	43.26	1.42	43.88
8	2.88	83.99	2.84	87.76
12	4.21	130.09	4.26	131.63
16	5.68	175.51	5.68	175.51
20	7.11	219.70	7.10	219.39

6. Change of Reduction Wave of dl-Allethrolone by Time.

The electrolytic solution of dl-allethrolone, which had the composition as shown in 1 of III, was left at 25 ± 0.2° C. for a certain period of time. Then the polarograms were taken, and the half-wave potentials and the wave heights were measured. The results are shown in Table 4.

Table 4

Wave Heights and Half-Wave Potentials of 16×10^{-4} *M* dl-Allethrolone of which The Electrolytic Solution is Left at 25 ± 0.2° C. for a Certain Period of Time.

	Time		
	30 min.	1 hr.	2 hrs.
Wave height, cm.	5.67	5.68	5.63
Half-wave potential, v.	−1.32	−1.32	−1.32

7. Influence of Allyl Acetone, Pyruvaldehyde, Ethyl-3-oxo-6-heptenoate, and 3-Hydroxy-8-nonene-2,5-dione on Reduction Wave of dl-Allethrolone.

Electrolytic solutions were prepared, each one of which contained dl-allethrolone and either one of allyl acetone, pyruvaldehyde, ethyl-3-oxo-6-heptenoate, and 3-hydroxy-8-nonene-2,5-dione (crude matter) in various proportions. The quantitative analyses of dl-allethrolone in these solutions gave the results as shown in Table 5 and 6.

These experiments were performed by the method and under the conditions described in 1 of III.

Table 5

Determinations of dl-Allethrolone in Synthetic Samples. 1

		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
dl-Allethrolone,	10^{-4} *M*	16.0	16.0	16.0	16.0	16.0	16.0	16.0
Allyl actone,	10^{-4} *M*		4.0	8.0	16.0			
Pyruvaldehyde,	10^{-4} *M*					4.0	8.0	16.0
Half-wave potential of dl-allethrolone, found,	v.	−1.32	−1.31	−1.31	−1.31	−1.31	−1.31	−1.31
Wave height, found,	cm.	5.68	5.62	5.64	5.65	5.68	5.68	5.67
Error,	%		0	0	0	0	0	0

Table 6

Determinations of dl-Allethrolone in Synthetic Samples. 2

		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
dl-Allethrolone,	10^{-4} *M*	16.0	16.0	16.0	16.0	16.0	16.0	16.0
Ethyl-3-oxo-6-heptenoate,	10^{-4} *M*		4.0	8.0	16.0			
3-hydroxy-8-nonene-2,5-dione*,	10^{-4} *M*					4.0	8.0	16.0
Half-wave potential of dl-allethrolone, found,	v.	−1.32	−1.31	−1.31	−1.31	−1.31	−1.31	−1.31
Wave height, found,	cm.	5.68	5.62	5.63	5.64	5.65	5.66	5.64
Error,	%		0	0	0	0	0	0

* The concentration of this is shown by assuming this as pure matter.

Table 7

Determinations of dl-Allethrolone in Technical Products and Analytical Values of Standard dl-Allethrolone Added to Those Technical Products

			No. 1*	No. 2*	No. 3*	No. 4**	No. 5**
Technical product	Technical product,	mg.	6.00	6.00	6.00	3.00	3.00
	Wave height, found,	cm.	3.60	4.11	5.60	7.01	7.02
	Concentration of dl-allethrolone, found,	10^{-4} *M*	10.14	11.58	15.77	19.75	19.77
	dl-Allethrolone, found, (I),	mg.	1.53	1.75	2.38	2.98	2.99
	dl-Allethrolone, found,	%	26	29	40	99	100
Standard dl-allethrolone added to technicial product	Technical product,	mg.	6.00	6.00	6.00		
	Standard dl-allethrolone, added, (II),	mg.	0.60	0.60	0.60		
	Wave height, found.	cm.	5.08	5.55	7.03		
	Concentration of dl-allethrolone, found,	10^{-4} *M*	14.31	15.63	19.80		
	dl-Allethrolone, found, (III),	mg.	2.16	2.36	2.99		
	Standard dl-allethrolone, found, (III−I=IV),	mg.	0.63	0.61	0.61		
	Difference between II and IV, (V),	mg.	+0.03	+0.01	+0.01		
	Error, (V/II×100),	%	+5	+2	+2		

* These products are undistilled matter. ** These products are distilled matter.

8. Results of Determination of dl-Allethrolone in Technical Products and Analytical Values of Standard dl-Allethrolone added to the Technical Products.

Technical products produced by various makers have been analysed by the method shown in I of III, and the polarograms and the results are shown in Fig. 7 and Table 7, respectively.

The analyses were conducted after adding some quantity of standard dl-allethrolone to the technical products of No. 1~No. 3. The results are shown in Table 7.

SUMMARY

1. The crude dl-allethrolone synthesized by the usual method was purified by column partition chromatography and standard dl-allethrolone was obtained.

2. When dl-allethrolone was reduced at dropping mercury electrode in the electrolytic solution of ethyl alcohol (50%), *M*/5 $(CH_3)_4$-NBr solution (10%), and Sörensen's buffer solution of pH 2.00 (40%), the typical reduction waves were obtained. The half-wave potential was −1.32 v. at 25 ± 0.2°C. in the solution.

3. The wave height of dl-allethrolone was proportional to the concentration.

4. When dl-allethrolone was reduced at different pH values, the reduction waves of various different types were obtained.

5. As the temperature increased, the half-wave potential of dl-allethrolone shifted to the negative potential, and the wave height increased proportionally.

6. The determination of dl-allethrolone by polarographic method was deviced 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.

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Errata

Vol.	Page	Line	Error	Correction
15	185	Fig. 2, Configuration VI'7	$\widehat{\text{pe}}$, p, p, p, p, e	$\widehat{\text{pe}}$, p, p, e, p, e
16	17	23(left side)	76.46	76.32
	19	25(left side)	76.34	76.32
17	110	30(right side)	16×10^{-4} *M*	omit
	111	28(left side)	opitcal	optical
	112	29(left side)	boling is	boiling it is
	112	35(right side)	$10^{-4}M$	$2\times10^{-3}M$
	113	23(left side)	Polarogrms	Polarograms
	113	14(right side)	allethrin, by	allethrin by
	114	23(left side)	case α-dl-	case of α-dl-
	120	34	ca. −1.72	ca. —1.27
	119	Table 7	10^{-4} *M*	10^{-3} *M*
	120	Table 8		
	120	Table 9		
	121	Table 10		