

of the two species of rice leaf-hoppers.

Unfortunately press of the great war made it practically impossible to make use of the necessary laboratory equipments such as constant temperature cabinet, low temperature cabinet, etc, which were indispensable for carrying out such ecological study as we had in mind. So, experiments were carried out under the room temperature. Some of the experiments, were carried out in cabinets which were heated and kept under nearly constant temperature during the night only.

Leaf-hoppers were reared in test tubes containing a rice plant cut in moderate length. The relative humidity in the rearing tubes was not controlled. However, owing to the small quantity of water at the bottom of the tube, the relative humidity was kept practically 100%.

The temperatures in the room and in the rearing cabinets were recorded using recording thermometers. The mean temperatures for the

egg, larval or for the imaginal periods, were calculated using the temperature records and the relationship between the temperature and the developmental stages was examined.

Owing to the difficulty mentioned above, the results obtained were far from being satisfactory. Therefore, definite conclusions can not be drawn yet.

Nevertheless, certain interesting ecological characters which seem to be in harmony with the popular name, "autumn leaf hoppers", have been found. For example, the rate of development, or rate of multiplication, of these two species does not decrease in the autumn in spite of quite marked fall of air temperature in the autumn.

As regards the hibernation of these two species, some experiments and field observations were made. The results however, are far from conclusive yet, and it is hoped that we shall be able to take up this study some time in future.

Studies on the Molecular Structures of BHC and its Related Compounds. III. On the Molecular Configurations of  $\gamma$ -BHC,  $\delta$ - and  $\epsilon$ -1,1,2,3,4,5,6-Heptachlorocyclohexane. Toshihiko OIWA, Ryoichi YAMADA and Minoru OHNO (Takei Laboratory, Institute for Chemical Research, Kyoto University) Received Jan. 27, 1951. *Botyu-Kagaku*, 16, 11 (1951).

## 2. BHC 及びその近縁物質の分子構造に関する研究. III.

$\gamma$ -BHC,  $\delta$ -及び  $\epsilon$ -1,1,2,3,4,5,6-Heptachlorocyclohexane の原子の立体配置に就て.

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先に中島及び著者の一人<sup>(1)</sup>は  $\gamma$ -BHC の塩素化反応, 脱塩酸反応及び脱塩酸産物の塩素化反応の検討から  $\gamma$ -BHC,  $\delta$ -1,1,2,3,4,5,6-heptachlorocyclohexane (mp 139~140°;  $\delta$ -hepta)<sup>(2)</sup>及び  $\epsilon$ -1,1,2,3,4,5,6,-heptachlorocyclohexane (mp 55~55.5°;  $\epsilon$ -hepta) の原子の立体配置を提案した。次で森野, 宮川及び著者等の一人<sup>(2)</sup>は双極子能率の研究から,  $\gamma$ -BHC の原子の立体配置を決定し, 有機化学的に得た  $\delta$ -及び  $\epsilon$ -hepta の原子の立体配置は双極子能率の結論と矛盾しないことを指摘した。 $\delta$ -及び  $\epsilon$ -hepta の分子構造に就てはこれら以外の報告には未だ接しないが,  $\gamma$ -BHC の分子構造に就てはこれのほかに G. W. van Vloten 等<sup>(3,4)</sup>及び J. M. Bijvoet<sup>(5)</sup>の X線解析の, 又 O. Bastiansen 等<sup>(6)</sup>の気体電子廻折からの研究がある。そしてこれらの  $\gamma$ -BHC の原子の立体配置はすべて同一の結論に達している。

著者等<sup>(7,8)</sup>は BHC 異性体及びそれらの近縁化合物の構造を塩素化反応を主とする有機化学の立場から研究しつつある。本報に於ては先に速報<sup>(9)</sup>した  $\epsilon$ -hepta 弱見の詳細, その後の  $\alpha$ -及び  $\gamma$ -BHC の塩素化反応に関する知見及びそれ等の実験結果を検討して決めた  $\gamma$ -BHC,  $\delta$ -及び  $\epsilon$ -hepta の原子の立体配置に就て報告する。

1.  $\gamma$ -BHC 及び Monochlorobenzene の塩素化物から  $\epsilon$ -hepta の単離確認。  $\gamma$ -BHC の塩素化物の polarogram から,  $\gamma$ -BHC を塩素化すると, 少くとも 2 つ以上のより高級な塩素化物に変化することを知った。この塩素化物から partition chromatography によつて融点 55~55.5°, 半波電位約 -0.9V, 双極子能率 2.22D<sup>(10)</sup>の無色柱状の結晶を分離した。この化合物の塩素含量は  $C_7H_6Cl_7$  と一致し, アルカリで脱塩酸すると融点 100~101° の hexachlorocyclohex-

ene<sup>(10)</sup>の異性体と共に1,2,3,5-tetrachlorobenzeneを生ずる。又一方 monochlorobenzene の塩素化物を蒸気蒸溜次で partition chromatography で分別して上述の融点 55~55.5° の結晶を得た。これらのことからこの融点 55~55.5° の化合物は 1,1,2,3,4,5,6-heptachlorocyclohexane (hepta) の一新異性体と考えられ、著者等は  $\epsilon$ -1,1,2,3,4,5,6-heptachlorocyclohexane と呼ぶことにした。

dioxane 溶液中で  $\epsilon$ -hepta に L-brucine を作用させて融点 54~55°, 比旋光度 -21.6° の結晶を分離した。この化合物の塩素含量は  $C_6H_5Cl_7$  と一致し、polarogram は元の  $\epsilon$ -hepta と全く同じであつた。これらのことからこの化合物は  $\epsilon$ -hepta の L- 体と考えられ、元の  $\epsilon$ -hepta そのものは DL- 体であると思われる。

2.  $\alpha$ -BHC の塩素化物中から  $\gamma$ -,  $\delta$ - 及び  $\epsilon$ -hepta の単離確認。吾々<sup>(8)</sup>は先に  $\alpha$ -BHC の塩素化物の polarograph 分析から  $\alpha$ -BHC を塩素化すると  $\gamma$ -1,1,2,3,4,5,6-heptachlorocyclohexane (mp 85~86°;  $\gamma$ -hepta) 及び  $\alpha$ -1,1,2,2,3,4,5,6-octachlorocyclohexane (mp 149~150°;  $\alpha$ -octa) が生成することを指摘し、実際にも  $\alpha$ -octa を単離確認した。その後再び  $\alpha$ -BHC の塩素化物を詳細に検討した。その結果  $\alpha$ -BHC を塩素化すると  $\gamma$ -hepta, 及び  $\alpha$ -octa 以外に  $\epsilon$ -hepta 及び  $\delta$ -hepta も生成することを赤外線分析から知り、次で partition chromatography によつて  $\gamma$ -,  $\delta$ - 及び  $\epsilon$ -hepta を分離した。尚その分別状態から、 $\alpha$ -BHC を塩素化して生成する hepta 異性体の大部分は  $\gamma$ -hepta であり、極く少量が  $\delta$ - 及び  $\epsilon$ -hepta であると思われる。

3.  $\gamma$ -BHC 並びに  $\delta$ - 及び  $\epsilon$ -hepta の原子の立体配置。 $\alpha$ -BHC の原子配置は既に第1報<sup>(8)</sup>で Fig. 1 の I であることを明かにした。この構造から生成し

得る hepta の理論異性体を示すと II, III 及び IV のようである。この中 II が  $\gamma$ -hepta であることは既に第2報で決めた。従つて残りの III 及び IV の中何れか1つが  $\delta$ -hepta であり、他の1つが  $\epsilon$ -hepta である。 $\epsilon$ -hepta は  $\gamma$ -BHC を塩素化しても得られるから、今 III 或は IV を誘導し得る BHC の異性体を考えて見る。cyclohexane 環を椅子型とした場合に考えられる BHC の16の異性体中 III 或は IV が生成する型は、I 以外では夫々 VII 及び V のみである。従つて V か VII の何れかが  $\gamma$ -BHC である。森野等<sup>(11)</sup>の指摘したように両者の双極子能率の計算値は 3.19~2.93D (V) 及び 1.88D (VII) であり、 $\gamma$ -BHC の実測能率は 2.80D である。故に V が  $\gamma$ -BHC である。光学的に VII では D- 及び L- 型が存在すると考えられるが V では考えられない。このことは  $\gamma$ -BHC の光学活性体を分割できなかつたこと云々実験結果<sup>(11)</sup>と矛盾しない。V から生成し得る hepta 異性体は IV, IV', VI 及び VI' であるが、その中 IV のみが  $\alpha$ -BHC から生成しうる。実験では  $\alpha$ -BHC 及び  $\gamma$ -BHC の塩素化によつて  $\epsilon$ -hepta のみが共に生成した。従つて IV が  $\epsilon$ -hepta であり、III が  $\delta$ -hepta である。

茲に明かにした  $\gamma$ -BHC 並びに  $\delta$ - 及び  $\epsilon$ -hepta の原子の立体配置は著者等<sup>(11)</sup>の先の提案と一致する。

第1報<sup>(8)</sup>、第2報<sup>(9)</sup>及び本報で著者等は  $\alpha$ -,  $\gamma$ -,  $\delta$ - 及び  $\epsilon$ -BHC,  $\alpha$ -,  $\gamma$ -,  $\delta$ - 及び  $\epsilon$ -hepta 並びに  $\alpha$ - 及び  $\beta$ -p-octa の原子の立体配置を明かにした。この過程に使用した他の研究者の実験的結論は次の2つである。即ち、(1) cyclohexane 環の構造は椅子型であると云う Hassel 等<sup>(12, 13, 14)</sup>の分子スペクトル及び電子廻折の結果、及び(2)  $\beta$ -BHC の構造は塩素原子が椅子型の cyclohexane 環の6つの e-bond と結合していると云う Dickinson 等<sup>(15)</sup>の X 線解析の結果である。

It has been already reported that by M. Nakazima and one of the present authors<sup>(1)</sup> the molecular configurations of  $\gamma$ -BHC,  $\delta$ -1,1,2,3,4,5,6-heptachlorocyclohexane (mp 139~140°;  $\delta$ -hepta) and  $\epsilon$ -1,1,2,3,4,5,6-heptachlorocyclohexane (mp 55~55.5°;  $\epsilon$ -hepta) were reported by investigating the chlorinations, dehydrochlorinations and chlorinations of dehydrochlorination compounds of  $\gamma$ -BHC and its related compounds. On the other hand, on the basis of the dipole moment measurements of the isomers of BHC and its related compounds the molecular configuration of  $\gamma$ -BHC has been assigned by Y. Morino, I. Miyagawa, and one

of the present authors<sup>(2)</sup>, and its configuration agreed with the conclusion reached by M. Nakazima et al.<sup>(1)</sup>. Moreover, it was elucidated that the molecular configurations of  $\delta$ - and  $\epsilon$ -hepta which were proposed by M. Nakazima et al.<sup>(1)</sup> did not conflict with the conclusions of the investigations of their dipole moments measurements. At present, there is no study of the molecular configurations of  $\delta$ - and  $\epsilon$ -hepta based on other standpoints. About the molecular configuration of  $\gamma$ -BHC, however, researches have been made by G. W. van Vloten, Ch. A. Kruissink, B. Strijk, and J. M. Bijvoet<sup>(3, 4)</sup> and J. M. Bijvoet<sup>(5)</sup> from the standpoint of the

X-ray diffraction measurement, and by O. Bas-tjansen, Ø. Ellefsen and O. Hassel<sup>(6)</sup> on the basis of the electron diffraction measurement. These several propositions on the molecular configuration of  $\gamma$ -BHC came to the same conclusion.

The authors<sup>(7, 8, 9)</sup> have been investigating the structures of BHC and its related compounds from the standpoint of chemical reactions. At this time, the authors are pleased to introduce the detailed account of the discovery of  $\epsilon$ -hepta from the chlorination product of  $\gamma$ -BHC which were explained briefly in some of our reports<sup>(9, 11)</sup> and the further information on the chlorination of  $\alpha$ - and  $\gamma$ -BHC, and to report on the determination of molecular configurations of  $\gamma$ -BHC,  $\delta$ -, and  $\epsilon$ -hepta as the result of the investigation of these experiments.

#### I. Isolation of $\epsilon$ -hepta from the Chlorination Product of $\gamma$ -BHC and Monochlorobenzene.

It was found by polarographic analysis that the chlorination product of  $\gamma$ -BHC consists of at least two of the more chlorinated substances. The colorless, columnar crystals which had melting point of  $55\sim 55.5^\circ$  and dipole moment of 2.2D<sup>(12)</sup>, were isolated from the chlorination product by partition chromatography. The chlorine content of this compound found agreed with the calculated value of  $C_6H_5Cl_7$ . The alkaline dehydrochlorination product of this compound was a mixture of an isomer of hexachlorocyclohexene (mp  $100\sim 101^\circ$ ;  $C_6H_4Cl_6$ ) and 1,2,3,5-tetrachlorobenzene (mp  $48\sim 49^\circ$ ;  $C_6H_2Cl_4$ ), etc. On the other hand, from the chlorination product of monochlorobenzene, first by steam distillation and then by partition chromatography, colorless columnar crystals were obtained of which melting point was  $55\sim 55.5^\circ$ . As the result of the mixing melting point method, it is known that this compound was the same as the compound having the melting point of  $55\sim 55.5^\circ$ , which was prepared from  $\gamma$ -BHC. The authors believe that this compound having the melting point of  $55\sim 55.5^\circ$  is a new isomer of 1,1,2,3,4,5,6-heptachlorocyclohexane (monochlorobenzene hexachloride; hepta) and hereafter this compound is called  $\epsilon$ -1,1,2,3,4,5,6-

heptachlorocyclohexane( $\epsilon$ -hepta). When  $\epsilon$ -hepta was reacted with L-brucine in dioxane, a new compound was separated. The melting point of this compound was  $54\sim 55^\circ$  and its specific rotation was  $-21.6^\circ$ . The chlorine content of this compound found agreed with the calculated value of  $C_6H_5Cl_7$ . From these results, this compound having the melting point of  $54\sim 55^\circ$  is supposed to be L- $\epsilon$ -hepta, and consequently, original  $\epsilon$ -hepta should be a DL-compound.

#### II. Isolation of $\gamma$ -, $\delta$ -, and $\epsilon$ -hepta from the Chlorination Product of $\alpha$ -BHC.

On the first paper<sup>(8)</sup>, it was found by the polarographic analysis of the chlorination product that when  $\alpha$ -BHC was chlorinated, it changed easily into  $\gamma$ -hepta and o-1,1,2,2,3,4,5,6-octachlorocyclohexane (mp  $149\sim 150^\circ$ ; o-octa) and also o-octa was isolated actually. After that the authors have studied on the chlorination product of  $\alpha$ -BHC by means of polarographic and infrared absorption analyses and organic chemical method with partition chromatography. From the infrared analysis of some of the fractions separated by partition chromatography, it was learned that  $\delta$ -hepta, which was isolated recently by M. Nakazima, T. Ohkubo, and Y. Katsumura<sup>(10)</sup>, and  $\epsilon$ -hepta were also produced from  $\alpha$ -BHC with  $\gamma$ -hepta and o-octa. Further, repeating the separation of the substances of these fractions, by partition chromatography and the purification of the separated matter by recrystallization,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -hepta were isolated. Judged from the state of each fraction separated by the partition chromatography, it is known that the greater part of hepta isomers produced is  $\gamma$ -hepta, and  $\delta$ - and  $\epsilon$ -hepta are only little.

#### III. Assignments of Molecular Configurations of $\gamma$ -BHC, $\delta$ -, and $\epsilon$ -hepta.

The molecular configuration of  $\alpha$ -BHC has been already determined in the first paper as is shown in I of Fig. 1. The possible isomers of hepta, which can be derived from this, are II, III, and IV. Since II has been assigned to be the molecular configuration of  $\gamma$ -hepta in the second paper<sup>(9)</sup>, one of the two forms left is of  $\delta$ -hepta, and

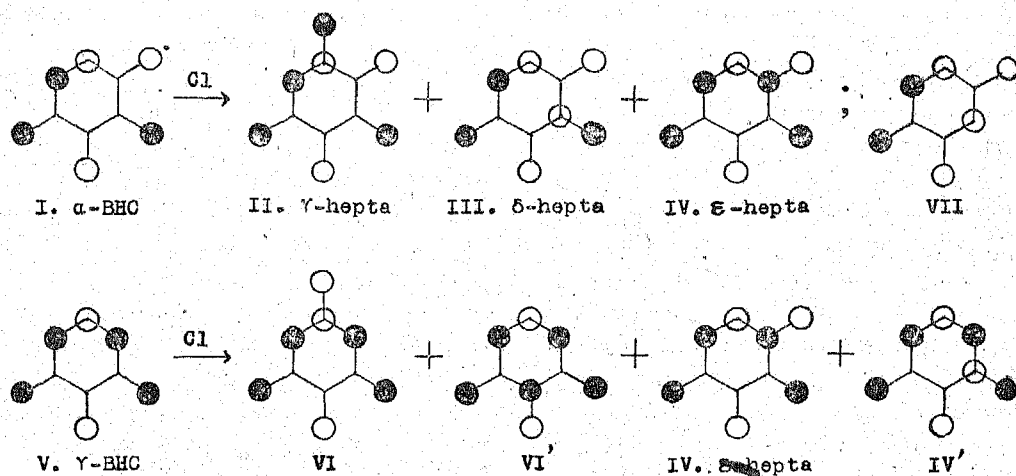


Fig. 1: Molecular Configurations of  $\alpha$ - and  $\gamma$ -BHC and Possible Isomers of 1, 1, 2, 3, 4, 5, 6-Heptachlorocyclohexane which can be produced from  $\alpha$ - and  $\gamma$ -BHC

In these figures the cyclohexane ring is represented by a hexagonal ring, chlorine atom in an equatorial bond (e-bond) by a short line, chlorine atom in a polar bond (p-bond) by a small circle on the hexagonal ring, and white and black circles represent chlorine atoms above and under the central plane.

the other of  $\epsilon$ -hepta. Now, taking into account the fact that the forms III and IV can be also derived from the forms VII and V of 16 possible isomers of BHC respectively, and the experimental result that  $\epsilon$ -hepta is also produced by chlorination of  $\gamma$ -BHC, it must be said that one of the two, V or VII, is the molecular configuration of  $\gamma$ -BHC. As has been pointed out by Y. Morino, I. Miyagawa, and T. Oiwa,<sup>(2)</sup> the calculated values of dipole moments of the two forms are 3.19~2.93D(V) and 1.85D(VII), and the experimental value for  $\gamma$ -BHC is 2.80D. Consequently, V should be the molecular configuration of  $\gamma$ -BHC. Besides, the existence of both D- and L-forms are possible in VII, but not in V. This does not conflict with the experimental result<sup>(11)</sup> that the optical active form of  $\gamma$ -BHC is not separated. The isomers of hepta which can be derived from V are IV, IV', VI, and VI', but among them only IV can be obtained by the chlorination of both  $\alpha$ - and  $\gamma$ -BHC. Therefore, the conclusion is that IV is  $\epsilon$ -hepta and III is  $\delta$ -hepta. Moreover, both D- and L-forms are possible in IV and this agrees completely with the experimental

result that optical active form of  $\epsilon$ -hepta is separated.

Thus the authors<sup>(7,8,9)</sup> succeeded in determining the molecular configurations of  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -BHC,  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -1, 1, 2, 3, 4, 5, 6-heptachlorocyclohexane and  $\alpha$ -octa and  $\beta$ -p-1, 1, 2, 3, 4, 4, 5, 6-octachlorocyclohexane (mp 265°;  $\beta$ -p-octa). The experimental results of other investigators which were referred to in the course of determining these molecular configurations were: 1) The conclusion of studies of electron diffraction measurement by O. Hassel et al.<sup>(12,13,14)</sup> that the cyclohexane ring is the chair-form. 2) The conclusion\* of x-ray analysis by R. G. Dickinson and C. Bilicke<sup>(15)</sup> that

\* Before the present authors set their hand to the study of BHC and its related compounds, this molecular configuration of  $\beta$ -BHC has been supported by O. Hassel and F. Naeshagen,<sup>(16)</sup> J. W. Williams, and J. M. Fogelberg,<sup>(17)</sup> H. Martine<sup>(18)</sup>, and E. Hetland<sup>(19)</sup> from the field of dipole moment study, and by O. Hassel and T. Taaland<sup>(20)</sup> on the basis of gaseous electron diffraction measurement, and had practically no room for doubt.

$\beta$ -BHC is formed with 6 chlorine atoms bonded to the 6 e-bonds\* of the cyclohexane ring.

The molecular configurations of  $\gamma$ -BHC,  $\delta$ -, and  $\epsilon$ -hepta determined here agree entirely with the ones proposed by M. Nakazima and T. Oiwa<sup>(1)</sup>.

## EXPERIMENTAL

### I. Polarographic and Infrared Absorption Analyses and Partition Chromatography.

Polarographic\*\* and infrared\*\*\* analyses were used as the supplement to the organic chemical procedures.

Experimental conditions of the polarographic analysis was nearly the same as in the case by M. Suzuki and M. Nakazima,<sup>(2)</sup> and is as follows:

Base solution: dioxane (40%) and 7.7%

(CH<sub>3</sub>)<sub>4</sub>NBr solution (10%), and Koltoff's

Buffer solution (pH=7), containing some

of gelatin as maximum suppressor (50%).

Before recording dissolved oxygen is removed from solution by a stream of hydrogen.

Recording range: -0.1~-2.0V. (N-calomel electrode)<sup>(3)</sup>

Temperature: 25° ± 0.1°

Galvanometer sensitivity: 3.09 × 10<sup>-8</sup> or 1.045 × 10<sup>-8</sup> A/mm/m

Qualitative analysis by the infrared absorption was done by Mr. K. Kuratani, Chemical Laboratory, Faculty of Science, Tokyo University, and the spectrophotometer used was of Baird make. The wave range measured was 5.3 $\mu$ ~16 $\mu$ . The sample was mixed thoroughly with paraffin oil in solid form.

Partition chromatography used was a modification of L. L. Ramsey's and W. I. Patterson's<sup>(4)</sup>, and was as follows:

Preparation of the partition chromatographic column: To 100 grams of silicic acid in a large mixing vessel, 10 grams of nitromethane was added 5 times, and mixed thoroughly after each addition. Then about 100 grams of petroleum ether (bp 6)~80°) was added 6 times, and mixed thoroughly until it became a slurry. The resultant slurry was poured into a glass tube (absorption tube). The size of this tube was 3 cm O. D. × 70 cm long and the constricted

end was plugged with a small piece of cotton wool, and on it a small perforated plate about 2.9 cm in diameter was placed. The tube was placed in a clamp on a ring stand and connected to a compressor air line through the pressure regulator and pressure was applied. When there was sufficient space in the tube, the rest of the slurry was poured in. When the silicic acid was so firm that it retained its shape on tipping, the pressure was released.

Procedure of separation: The sample was dissolved in the petroleum ether reagent which was saturated with nitromethane. This solution was transferred to the absorption column, carefully so that the top of the silicic acid was

\* This is shown by simple notation of p (polar) and e (equatorial) proposed by C. W. Beckett, K. S. Pitzer, and R. J. Spitzer (J. Am. Chem. Soc., 69, 1488 (1947)).

\*\* Of the five isomers of BHC, four of hepta, four of octa;  $\gamma$ -BHC,  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -hepta and o-octa are reduced at a dropping mercury cathode and the half wave potentials of these compounds are about -1.15V<sup>(21)</sup>, -0.94 V<sup>(22)</sup>, -0.8 V<sup>(23)</sup>, -0.95 V, -0.9 V, and -0.15 V<sup>(23)</sup> respectively. There are slight differences among these potentials, and also the forms of waves of these compounds are rather different from one another. By comparing these potentials, it is known that the half wave potentials of the chlorine derivatives of cyclohexane decrease as their chlorine content increases.

\*\*\* The conclusion based only on polarographic analysis often lacks accuracy, because half wave potentials of the compounds mentioned in the above note, especially of hepta, are very close with one another, and there is possible existence of unknown derivatives of which half wave potentials are close to those of the above compounds. Therefore, infrared absorption analysis was used to trace these compounds qualitatively.

Infrared absorption spectra of isomers of BHC, hepta, and octa used for the analysis are those shown in the following report which will be published soon.

K. Kuratani: Report of the institute of Science and Technology, University of Tokyo, 5, (1951).

not disturbed. The pressure line was connected to the column and sufficient pressure (3-7 lbs. per square inch) 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 petroleum ether reagent and the pressure was applied again. After a certain volume of percolate solution had passed through the column, the collection of 20cc fraction was begun, and the solvent was removed. The fractions were collected until no significant amount of material came through the column.

**II. Isolation of  $\epsilon$ -hepta from the Chlorination Product of  $\gamma$ -BHC.**

Using the same apparatus and by the same method, described in the first paper<sup>(9)</sup>, 13 grams of  $\gamma$ -BHC (mp 112-112.5°) was photochlorinated in 400 grams of carbon tetrachloride solution containing 16 grams of chlorine at 46° over a period of 1.5 hours. As soon as the reaction was finished the solvent was removed by distillation on steam bath and then under diminished pressure. Finally 18 grams of the residual oily substance was obtained. The polarogram of it is shown in II of Fig.2.

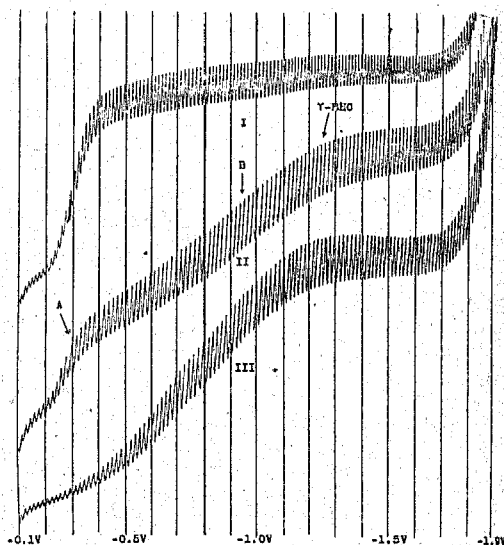


Fig.2 : Polarograms

- I. 1,2,3, 4,5,6- hexachlorocyclohexene (mp 100~101°) Conc. :  $4 \times 10^{-4}$  mol
- II. chlorination product of  $\gamma$ -BHC
- III.  $\epsilon$ -1,1,2,3,4,5,6-heptachlorocyclohexane Conc. :  $4 \times 10^{-4}$  mol

By observing this polarogram, it was found that  $\gamma$ -BHC was changed into at least two of the more chlorinated compounds, e. g. A and B. Five grams of this oily matter was dissolved in 40 cc petroleum ether reagent and

Table. 1 : Illustrating the Collection of Percolate Fractions and their Classification from one Chlorination Product of  $\gamma$ -BHC (5.1 grams of petroleum ether soluble material placed on the column)

Fraction		Description	Classification
No.*	Weight g.		
1	0.21	oil; slightly colored	unknown
2	0.23	//	//
3	0.36	//	//
4	0.34	//	octa
5	0.37	//	//
6	0.39	//	a mixture of octa and hepta
7	0.34	crystals containing some oil; colorless	a mixture of hepta and a little octa
8	0.38	//	hepta
9	0.20	//	//
10	0.31	//	//
11	0.32	oil; slightly colored	a mixture of hepta and $\gamma$ -BHC
12	0.33	oily solid; colorless	//
13-16	1.12	crystals; colorless	$\gamma$ -BHC

\* 20cc fraction, No.1 being 120-140cc fraction

transferred into partition column. The result of the separation procedure is shown collectively in Table 1.

After repeating 9 times the same procedure with 46 grams of other oily substance, the fractions corresponding to the fractions No. 7, 8, 9, and 10 of this table were combined into one, and 12.7 grams of rough crystals of which melting range was 45~49° were obtained. These crystals were refractionated in a fresh column of the same size, and the middle fractions were collected and recrystallized 6 times from isopropyl alcohol. Thus 7.6 grams of crystals were obtained of which melting point was 55~55.5°, half wave potential was about -0.9V, and dipole moment was 2.20 D<sup>29</sup>. The polarogram of this compound is shown in III of Fig. 2 and chlorine analysis gave the following results:

	Sample(mg.)	AgCl(mg.)	Cl(%)
Found	No. 1	21.3	65.6
	No. 2	22.6	69.8
Calcd.	C <sub>8</sub> H <sub>7</sub> Cl <sub>7</sub> .....		76.46

### III. Isolation of ε-hepta from the Chlorination Product of Monochlorobenzene.

One hundred millilitre of 1% NaOH solution was added to 200 grams of monochlorobenzene in a flask, then the vessel was cooled by ice-water, and chlorine was applied slowly over a period of 2 hours with strong stirring in the sun, while more 100 cc of 1% NaOH solution was dropped over the reaction. When the reaction was over, the oily matter was separated and about 50 grams of unreacted monochlorobenzene was removed by distillation. After one night's cooling off, the produced crystals (mainly of β-p-octa and α-hepta) were separated, and the unreacted matter was removed at a diminished pressure. (The total of the unreacted matter was 117 grams.) Thus, 203.5 grams of oily substance was obtained. To this substance, 40 cc of petroleum ether was added, and dissolved by heat, then cooled for one night and the produced crystals (chiefly of α-hepta) was separated from mother liquid. This liquid was steam distilled, and 16.5 grams of oily substance of middle fractions were

obtained. Ten millilitre of ethyl alcohol was added to this, cooled, and then the produced crystals (chiefly of α-hepta) were separated. The mother liquid was refractionated by the partition chromatography, and the fractions which were supposed to be of ε-hepta were collected, and recrystallized by isopropyl alcohol 3 times, and 1.12 grams of crystals were obtained of which melting point, was 55~55.5°, half wave potential was about -0.9V. This did not show the depression of melting point when mixed with ε-hepta which had been obtained by the chlorination of γ-BHC, and it was proved that these two substances were one and the same.

### IV. Isolation of an Isomer of 1,2,3,4,5,6-Hexachlorocyclohexene and 1,2,3,5-Tetrachlorobenzene from the Alkaline Dehydrochlorination Product of ε-hepta.

Four hundred and fifty grams of acetone was placed in a flask and 3 grams of ε-hepta was dissolved in it. Five hundred and fifty millilitre of Koltoff's buffer solution (pH=10) was added slowly over a period of 30 minutes with continuous stirring, while the temperature of the reaction was held at 30° by means of a water thermostat. The reaction was then stopped by the addition of a certain amount of N-HCl solution. The acetone was removed by steam distillation and the residual mixture was extracted with ether. Thus 1.9 grams of oily substance containing some crystals was obtained. This substance was dissolved in 20 cc of the petroleum ether reagent and transferred into partition column. The result of the separation is shown collectively in Table 2.

The fractions No. 2 (mp 40~43°) and 3 (mp 30~32°) of this table were combined and purified 4 times from isopropyl alcohol. Thus, 0.12 gram of crystals of which melting point was 48~49° were obtained. The chlorine analysis gave the following results:

	Sample(mg.)	AgCl(mg.)	Cl(%)
Found	No. 1	19.8	52.3
	No. 2	21.3	56.8
Calcd.	C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> .....		65.71

From these this compound was proved to be 1,2,3,5-tetrachlorobenzene.

Table. 2 : Illustrating the Collection of Percolate Fractions and their Classification from one Dehydrochlorination Product of  $\epsilon$ -1,1,2,3,4,5,6-Heptachlorocyclohexane (1.9 g. of petroleum ether soluble material placed on the column)

Fraction		Description	Classification
No. *	Weight g.		
1	trace	oil; slightly colored	unkown
2	0.12	solution; colorless	tetrachlorobenzene
3	0.16	“	a mixture of tetrachlorobenzene and a little hexachlorocyclohexene
4	0.24	solid; colorless	a mixture of tetrachlorobenzene and hexachlorocyclohexene
5	0.27	crystals; colorless	hexachlorocyclohexene
6	0.26	solid; colorless	a mixture of hexachlorocyclohexene and $\epsilon$ -hepta
7	0.24	oil; slightly colored	“
8	0.18	crystals; colorless	$\epsilon$ -hepta
9	0.13	“	“
10	0.06	oil; slightly colored	unkown
11	trace	“	“

\* 20cc fraction, No.1 being the 140-160cc fraction

The fractions No.4 (mp 70~90°) and 5(mp 80~90°) of Table 2 were combined and recrystallized 4 times from isopropyl alcohol. Thus, 0.22 gram of crystals were obtained of which melting point was 100~101° and half wave potential was about -0.3V. The polarogram of it is shown in I of Fig. 2. The chlorine analysis gave the following results:

	Sample(mg.)	AgCl(mg.)	Cl(%)
Found	No. 1 22.4	66.3	73.21
	No. 2 19.7	58.8	73.87
Calcd.	C <sub>6</sub> H <sub>4</sub> Cl <sub>6</sub> .....		73.08

This compound did not show the depression of the melting point when mixed with an isomer of 1,2,3,4,5,6-hexachlorocyclohexene of mp 100~101° isolated recently by M. Nakazima, T. Ohkubo, and Y. Katsumura<sup>(10)</sup>, which showed, therefore, that the two compounds were the same.

The fractions No. 8(mp 46~48°) and 9(mp 49~50°) were combined and recrystallized 3 times from isopropyl alcohol and then 0.09 gram of unreacted  $\epsilon$ -hepta was obtained.

#### V. Separation of L- $\epsilon$ -hepta.

Optically active  $\alpha$ -BHC is successfully separated by S. J. Cristol<sup>(11)</sup>. The authors applied his method for the separation of L- $\epsilon$ -hepta.

Five grams of  $\epsilon$ -hepta, 12.4 grams of

L-brucine and 50 cc of dioxane were allowed to stand at room temperature for 6 days. The alkaloid and alkaloid hydrochloride were removed by washing with water and dilute acid. The mixture was extracted with ether and 3.12 grams of oily substance was obtained. This was separated by the partition chromatography and the result is shown collectively in Table 3.

The products of fractions No.2 and 3 were combined and recrystallized from isopropyl alcohol 5 times. Thus, 0.091 gram of crystals were obtained, of which melting point was 48~49°. This compound did not show the depression of melting point when mixed with 1,2,3,5-tetrachlorobenzene isolated above.

The products of fractions No.4 and 5 were combined and recrystallized 5 times from isopropyl alcohol. Then 0.082 gram of crystals were obtained, of which melting point was 100~101° and this compound did not show the depression of melting point when mixed with an isomer of 1,2,3,4,5,6-hexachlorocyclohexene of mp 100~101° described above.

The products of the fractions No. 6, 7, and 8 were combined and recrystallized from isopropyl alcohol 5 times. Then 0.41 gram of crystals of mp 53~54° were obtained, and its



Table.3 : Illustrating the Collection of Percolate Fractions and their Classification from one Product obtained by Reacting  $\epsilon$ -hepta with L-Brucine (3.12 g. of petroleum ether soluble material placed on the column)

Fraction		Description	Classification
No. *	Weight g.		
1	trace	oil; slightly colored	unknown
2	0.21	“	tetrachlorobenzene
3	0.26	solution; slightly colored	tetrachlorobenzene and hexachlorocyclohexene
4	0.3	oil; colorless	hexachlorocyclohexene and a little $\epsilon$ -hepta
5	0.31	crystals, containing some oil; colorless	hexachlorocyclohexene and $\epsilon$ -hepta
6	0.37	oily solid; colorless	$\epsilon$ -hepta and a little hexachlorocyclohexene
7	0.33	“	$\epsilon$ -hepta
8	0.29	“	“
9	0.37	“	“
10	0.21	“	“
11-16	trace	oil; slightly colored	unknown

\* 20cc fractions, No.1 being 120-140cc fraction polarogram was the same as that of original  $\epsilon$ -hepta. The specific rotation and the chlorine analysis were as follows:

$$[\alpha]_{D}^{23} \text{Hg:5461\AA} = -21.6^\circ$$

	Sample(mg.)	AgCl(mg.)	Cl(%)
Found No.1	21.9	67.5	76.29
No.2	20.2	60.3	76.68
Calcd.	C <sub>6</sub> H <sub>5</sub> Cl <sub>7</sub> .....		76.34

These results indicate that this compound is

L- $\epsilon$ -hepta.

VI. Isolation of  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -hepta from the Chlorination Product of  $\alpha$ -BHC

In exactly the same way as in the case of  $\gamma$ -BHC, 13 grams of  $\alpha$ -BHC was chlorinated and 17.8 grams of oily substance was obtained. Six comma five grams of this oily substance was separated by the partition chromatography, and the result is collectively shown in Table 4.

Table. 4 : Illustrating the Collection of Percolate Fractions and their Classification from one Chlorination Product of  $\alpha$ -BHC (6.5 g. of petroleum ether soluble material placed on the column)

Fraction		Description	Classification
No. *	Weight g.		
1	0.31	crystals, containing some oil; colorless	a mixture of nona** and a little o-octa
2	0.42	crystals, containing some oil; colorless	a mixture of nona and o-octa
3	0.40	“	a mixture of nona and o-octa
4	0.46	“	a mixture of nona, o-octa, and $\gamma$ -hepta
5	0.49	oil; colorless	a mixture of nona, o-octa, and $\gamma$ -hepta
6	0.43	crystals; colorless	a mixture of $\gamma$ -hepta and o-octa
7	0.44	crystals; slightly colored	a mixture of $\gamma$ -hepta and a little o-octa
8	0.39	oil, containing some crystals; slightly colored	a mixture of $\alpha$ -BHC and $\gamma$ - and $\epsilon$ -hepta
9	0.44	“	“
10	0.47	solid, containing some oil; colorless	a mixture of $\alpha$ -BHC and $\gamma$ - and $\delta$ -hepta
11	0.40	solid, containing some oil; slightly colored	“
12	0.39	“	“
13-15	0.79	crystals; colorless	$\alpha$ -BHC

\* 20cc fraction, No.1 being 12)-140cc fraction

\*\* nona (nonachlorocyclohexane)

Further, other 95 grams of the oily substance was separated in the same way. The fractions corresponding to the fractions No.6 and 7 were combined into one and 15.05 grams of rough crystals of which melting range was 53~56° were obtained. These crystals were recrystallized 6 times from isopropyl alcohol and once from methyl alcohol and 1.90 grams of crystals were obtained of which melting point was 85~86° and half wave potential was about -0.8 V. This compound did not show the depression of melting point when mixed with  $\gamma$ -hepta which was synthesized from monochlorobenzene<sup>(25)</sup>.

The fractions corresponding to the fractions No.8 and 9 of Table 4 were combined into one and 13.41 grams of oily substance was obtained. This oily substance was refractionated in the fresh column, and the middle fractions were collected. The infrared absorption spectrum of this substance is Sample.2 of Fig. 3.

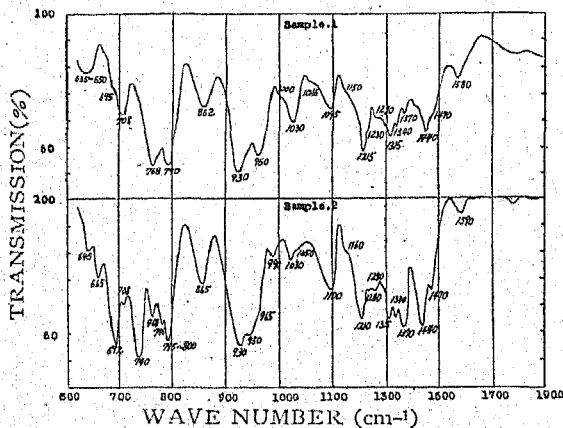


Fig.3: Infrared Absorption Spectra of Substance of Percolate Fractions

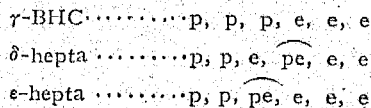
This curve shows the characteristic absorptions of  $\epsilon$ -hepta, beside of  $\gamma$ -hepta, and consequently the existence of the considerable amount of  $\epsilon$ -hepta. The substance was refractionated in the fresh column, and the middle fractions were collected. Then the substance was fractionally recrystallized 6 times from isopropyl alcohol and 1.56 grams of crystals were obtained of which melting point was 55~55.5° and half wave potential was about -0.9 V. This compound did not show the depression of

melting point when mixed with  $\epsilon$ -hepta which had been obtained by chlorination of  $\gamma$ -BHC.

The fractions corresponding to the fractions No.10, 11, and 12 were combined into one and 21.55 grams of solid was obtained. This solid was refractionated in a fresh column and the middle fractions were collected and 13.93 grams of solid was obtained. The infrared absorption spectrum of this substance is Sample.1 of Fig. 3. This curve shows, beside the absorptions of  $\gamma$ -hepta, the characteristic absorption of  $\delta$ -hepta and consequently the existence of small amount of  $\delta$ -hepta. The substance was refractionated 3 times in the fresh column. The fractions which were supposed to consist mostly of  $\delta$ -hepta were collected, and fractionally recrystallized 5 times from isopropyl alcohol and 0.97 gram of crystals were obtained of which melting point was 139~140° and half wave potential was about -0.95V. This compound did not show the depression of melting point when mixed with  $\delta$ -hepta which was prepared from  $\gamma$ -BHC by dehydrochlorination and then by chlorination<sup>(10)</sup>.

### CONCLUSION

1. A new isomer of 1,1,2,3,4,5,6-heptachlorocyclohexane ( $\epsilon$ -form) of which melting point was 55~55.5° was obtained by the chlorination of  $\gamma$ -BHC and monochlorobenzene.
2. An isomer of 1,2,3,4,5,6-hexachlorocyclohexene of which melting point was 100~101° was isolated when  $\epsilon$ -hepta was dehydrochlorinated by alkaline solution.
3. A levorotatory form of  $\epsilon$ -hepta was separated by reacting  $\epsilon$ -hepta with L-brucine.
4.  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -1,1,2,3,4,5,6-Heptachlorocyclohexane were isolated from the chlorination product of  $\alpha$ -BHC.
5. Molecular configurations of  $\gamma$ -BHC,  $\delta$ -, and  $\epsilon$ -1,1,2,3,4,5,6-heptachlorocyclohexane were determined by investigating the chlorination of  $\gamma$ - and  $\alpha$ -BHC and their chlorine configurations are as below:



## ACKNOWLEDGEMENT

We wish to express our appreciation to assistant professor M. Nakazima for his kind advice and to Prof. Y. Morino, Chemical Laboratory, Faculty of Science, Tokyo University, for his instruction. We are also deeply indebted to Mr. K. Kuratani, Chemical Laboratory, Faculty of Science, Tokyo University, for his assistance in infrared analysis.

The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the authors' thanks are due.

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Studies on the Ecology of Japanese Mosquitoes. 2. On the Marsh Mosquitoes, *Mansonia*. Yukio Shogaki (Kyoto, 35th Stat. Hospital, Mal. Surv. Sect.) Received Jan. 31, 1951. *Botyu-Kagaku* **16**, 1, 1951. (With English résumé)

3. 日本産蚊族の生態学的研究. 2. 日本産ヌマカ属 *Mansonia* の生態に就て

正垣幸男(京都・米軍第35ステーション ホスピタル・マツリヤ研究室) 26. 1. 31 受理

筆者は昭和21年(1946)以来京都に進駐せる米軍第207部隊(207th Mal. Surv. Det.)の命令で日本産蚊族の調査に従事して居るが、此処に筆者の採集せるヌマカ属 *Mansonia* で其の幼虫が特異な形態と習性を持つアシマダラスマカ *Mansonia uniformis* (THEOBALD, 1901) とケンイロスマカ *M. ochracea*

(THEOBALD, 1903) の2種に就て報告したい。

I. アシマダラスマカ *Mansonia uniformis* (THEOBALD, 1901)

成虫の全身特に脚の腿、脛節に多くの白斑があり、其の幼虫の棲息水域がマコモ、ドクゼリ、蓮等のある沼沢であり、随つて成虫も池沼畔、湖岸等の低濕地域