STUDIES ON THE HYDROGENATION AND DEHYDROGENATION OF PYRETHROSIN

By

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INTRODUCTION

Pyrethrosin, a white crystalline compound from pyrethrum flowers, was first isolated in 1890-91 (1,2). Since then it has been worked on sporadically by several investigators interested in insecticidal research (3,4,5,6). In 1937, a still residue obtained by McCormick and Company, Baltimore, Maryland, during the extraction of pyrethrum insecticides was identified by Haller and Rose as pyrethrosin (4). This still residue is the most important source of pyrethrosin. The Government Laboratories in 1941 abandoned further work on pyrethrosin after the publication of a paper on the azulene obtained from pyrethrosin (6). The work was relinquished because of the insecticidal inertness of pyrethrosin and the problem was turned over to the Chemistry Department of the University of Maryland. Last year, Dr. W. A. Stanton worked on the problem of the structure of pyrethrosin in this laboratory. His work (7) indicated that the complexity of pyrethrosin demanded that something be known of its basic carbon skeleton before further work would prove profitable. Since dehydrogenation studies have so often proved to be of value in elucidation of structure of complex natural products, the dehydrogenation of pyrethrosin was undertaken by the author with the hope that such work would lead to the basic structure of pyrethrosin. Early in this dehydrogenation work the need arose for stabilization of the molecule of pyrethrosin so that less decomposition would occur during dehydrogenation. This necessity lead to the hydrogenation studies.

EXPERIMENTAL PART

Isolation and Physical Properties of Pure Pyrethrosin

Isolation

At present the best source of pyrethrosin is the still residue furnished by McCormick and Company. The following directions describe utilization of this still residue to obtain pure pyrethrosin. These directions are modifications of unpublished methods of M. S. Schechter (8).

1750 g. of crude material, from McCormick and Company High Velocity Still, was dissolved in 14 liters of ethyl acetate by refluxing the material with the ethyl acetate for one hour. The hot ethyl acetate solution was then filtered through a small layer of glass wool in a large funnel to remove the bulk of the insoluble impurities. Filter-Cel was then added to the hot solution and the mixture was filtered on a large Buchner funnel by slight suction. Too much suction will evaporate the ethyl acetate and cause the pyrethrosin to crystallize in the pores of the filter.

The filtrate was cooled in an ice bath and the pyrethrosin which crystallized was filtered off on a Buchner funnel. The mother liquors were evaporated further; and successive crops of crystals were removed until the volume was about 1.5 liters, when the mother liquor was too syrupy for further crystallization. From the 1750g. of crude pyrethrosin, 870 g. of fairly pure pyrethrosin was obtained.

The pyrethrosin was further purified by crystallization from ethyl alcohol and ethyl acetate. 4 liters of ethyl alcohol and

500 ml. of ethyl acetate were used as solvent for each 300 g. of fairly pure pyrethrosin. 10 g. of charcoal was added to this solution to remove the brown-yellow color present.

The hot solution containing the 870 g. of pyrethrosin, 12.6 liters of ethyl alcohol, 1450 ml. of ethyl acetate, and 29 g. of charcoal was filtered through a fluted funnel to remove the charcoal. The pyrethrosin crystallized on cooling the filtrate. Successive crops of pyrethrosin were removed by further evaporation of the solvent until it was finally concentrated to one liter. In this way 780 g. of pure pyrethrosin (m.p. 200-202°) was obtained.

Rod-shaped Form of Pyrethrosin

Pyrethrosin dissolved in alcohol and allowed to cool slowly without stirring will frequently come down in long rods which melt at 201°. If an alcohol solution of these rods was seeded with the diamond-shaped form (really an octahedron) the diamond-shaped form separated on crystallization with stirring, and it too, melted at 200-201°. (The melting point of pyrethrosin must be gotten by raising the temperature rapidly until about 20° below the melting point. If the temperature is raised too slowly the material becomes glassy before it melts and does not melt completely at even as high a temperature as 220°)

After standing six months, the rod-shaped form could be seen to be breaking out with small diamond-shaped particles. It is assumed therefore, that the diamond-shaped form is the more stable at room temperature.

Solubility

Pyrethrosin is fairly soluble in hot benzene, 9.6 g./100 ml. of benzene at the boiling point of benzene.

Dehydrogenation of Pyrethrosin with Palladium on Charcoal

Preparation of the catalyst

A palladium on charcoal catalyst was prepared according to Linstead's modification (9) of the catalyst preparation of Zelinski and Turowa-Pollak (10). The following quantities were used: 5.5 g. of palladium (II) chloride was dissolved in 5 ml. of concentrated hydrochloric acid and then diluted with 300 ml. of distilled water. 10 g. of wood charcoal (nitric acid treated and washed free of nitrates) was allowed to soak in the palladium (II) chloride solution with 17 ml. of forty per cent formaldehyde (formalin) for half an hour. This mixture was reduced at room temperature by rapidly adding 38 ml. of fifty per cent sodium hydroxide with stirring. The catalyst was filtered on a Buchner funnel and washed with hot water until neutral. It was then washed with 100 ml. of ten per cent acetic acid. The catalyst was washed neutral again with hot water following the acetic acid wash, and was dried over phosphoric anhydride in a vacuum dessicator. The catalyst contains about twenty-five per cent of palladium. The catalyst could not be dried at 120° as done by Zelinski and Turowa-Pollak (10) for it would catch fire.

A test run with tetralin showed that 1 g. of the catalyst was active enough to dehydrogenate 9.7 g. (10 ml.) of tetralin in the liquid phase at 245° in seven hours.

Experiment 1

10 g. of pyrethrosin was thoroughly mixed with 1 g. of palladium on charcoal and placed in a flask so arranged that a carbon dioxide stream could sweep across the material. Joined to the ground glass neck of the flask was a long tube of glass serving as an air condenser. A side arm sealed to the top of this tube lead to a Dry Ice-alcohol trap. The gases were then passed through fifty per cent potassium hydroxide and collected in a large flask. The water displaced from this flask was measured and served in determining the volume of gas collected. The reaction flask was heated by a Wood's metal bath to the desired temperature.

TABLE I

Dehydrogenation of Pyrethrosin by Palladium on Charcoal

Time (minutes)	Temperature (°C.)	Volume of gas (ml.)
0	30	0
51	300	0
131	321	40
266	340	240
326	327	270
386	316	295
456	305	340
511	334	360
566	323	370
626	328	380
836	355	535
1035	280	625
1226	335	655
1301	310	662
1406	324	678

In the Dry Ice-alcohol trap was collected about 2-3 ml. of acetic acid. The acetic acid was identified by its p-phenylphenacyl ester m. p. 111.5°; literature value 111°, mixed melting point with known ester of acetic acid 111-111.5°. Above the acetic acid in the trap

was a small layer of an intensely blue compound. An attempt to isolate the blue component was a failure.

The residue in the reaction flask was black and hard. It was chipped out of the flask and the chips were extracted with a mixture of benzene and petroleum ether (90-100°). On cooling of the solution a brown solid separated from the fluorescent solution. The brown solid was soluble in benzene, toluene, and carbon tetrachloride. It was thrown out of these solutions by addition of petroleum ether. Attempts to purify the material by this method or by crystallization were failures.

The benzene-petroleum ether solution was then extracted with sodium bicarbonate solution, sodium hydroxide solution, and eighty-five per cent phosphoric acid successively and the solvent was evaporated. The residue from this treatment was a brown gummy material which resisted crystallization.

The sodium bicarbonate solution was acidified and extracted with ethyl ether. The residue after removal of the ether was minute in quantity although there were apparently a few white crystals present.

The sodium hydroxide solution was extracted in the same manner after acidification. On evaporation of the ether, about 0.5 ml. of an oily brown-red residue was obtained which had a phenolic odor. This fraction was heated with 1.0 g. of sodium acetate and 15 ml. of acetic anhydride for four hours on a steam bath. The solution was poured into 100 ml. of ice water where it remained as a milky white cloudiness. This suspension was neutralized with sodium hydroxide and extracted with ether. After evaporation of the ether a brown

solid remained. This solid was soluble in alcohol and did not precipitate on dilution of the alcohol. The solid could not be crystallized from toluene or carbon tetrachloride.

The phosphoric acid extraction was diluted with water and extracted with ether. After evaporation of the ether, a brown tarry gum remained.

Experiment 2

15 g. of pyrethrosin and 3 g. of palladium on charcoal was thoroughly mixed before being placed in the reaction flask. The same apparatus was employed; but the gas was not collected. The time of heating was twenty-four hours and the temperature was 330° ±20.

Acetic acid, with a blue layer floating on it, was again present in the trap. Ether was added to extract the blue color and an intense blue solution resulted. This solution of ether was dissolved in eighty-five per cent phosphoric acid. The phosphoric acid turned a golden brown and no color appeared in the petroleum ether which was used to wash the phosphoric acid. After several washes with petroleum ether, the phosphoric acid was diluted with water under a layer of ether. The ether became blue and the phosphoric acid layer became clear. The ether was evaporated and about 0.1 ml. of a deep blue oil remained.

The material remaining in the reaction flask was distilled under 2 mm. of mercury pressure. It did not distill until the temperature of the bath was 300° and then it came over as a viscous light blue oil. The color changed to a light brown as the temperature was raised. The distillation was stopped at a bath temperature of 350° as nothing

more seemed to be coming over. This distillation was done under an atmosphere of carbon dioxide.

The light brown oil obtained on distillation changed to a deep red-brown on standing. It did not seem to form a picrate from an alcohol solution; nor did it give a color with iron (III) chloride. The oil was insoluble in water and ten per cent sodium bicarbonate. In ten per cent sodium hydroxide it formed a blue-green color and most of the material remained as a brown oil. It was insoluble in dilute hydrochloric acid and turned green in concentrated hydrochloric acid. It was soluble in concentrated sulfuric acid with a green color, and the oil was thrown down on dilution of the sulfuric acid.

This brown oil was made alkaline and steam distilled. A water white oil was obtained in the distillate, which toward the end of the distillation had become a light yellow. The oil was extracted from the water with pure ether and the ether was evaporated. About 1 ml. of a light red-yellow oil was obtained. The material burned with a smoky yellow flame. By distillation of this oil, three fractions were obtained which boiled at 270-280°, 280-290°, and 300-320°. The first fraction was slightly the largest and the last was smallest. The refractive index of the fraction which boiled at 300-320° was $n_D = 1.572$.

The three fractions were combined and dissolved in petroleum ether and chromatographed through Brockmann's alumina. The material so obtained was clear light yellow and when dissolved in methyl alcohol and treated with a saturated solution of picric acid in

methyl alcohol, it gave an orange-red picrate which had a melting point of 58-68° under the hot stage microscope. Attempts to recrystallize the picrate unsuccessful, although it did seem to come out from ethyl alcohol nicely. However the picrate seemed too soluble in methyl alcohol and ethyl alcohol, and separation from the picrate was uncertain.

The picrate was dissolved in a little benzene and petroleum ether and chromatographed through alumina. The solvent was removed and an analysis was run on the product.

C* = 92.39% H = 9.19%

The solution remaining after steam distillation was acidified and extracted with ether and the ether evaporated. A dark red liquid smelling like rosin oil was obtained. The red liquid dissolved in ten per cent sodium hydroxide to give a green color. About 2.0 g. of the red liquid, dissolved in a minimum of ten per cent sodium hydroxide, was shaken in the cold with 12 ml. of dimethyl sulfate for half an hour and allowed to stand overnight. In the morning a brown-red oil had settled to the bottom. This oil was washed with sodium hydroxide solution and water and then steam distilled. On distillation the dimethyl sulfate came over first and settled to the bottom, later a light-yellow oil came over which floated on the water. A red gum remained in the flask which dissolved in benzene and petroleum ether. This solution was dried over calcium sulfate and was chromatographed through alumina. The solvent was evaporated leaving a light-yellow oil. This oil when dissolved in ethyl alcohol and cooled yielded a light-yellow precipate. The compound apparently melted around 10° for it turned to an oil on warming to room temperature.

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* The author is indebted to Dr. W. A. Stanton for this analysis.

Experiment 3

60 g. of pyrethrosin was thoroughly mixed with 7.7 g. of palladium on charcoal and heated for sixteen hours at 320-330°. The same apparatus was employed, but the gas was not collected.

The material in the flask was distilled at 1-3 mm. pressure and the bath temperature was finally raised to 360°. The distillate amounted to 10 ml., the first 5 ml. of which was liquid and blue in color and the last 5 ml. of which was a yellow-green semi-liquid gel. The Dry ice-alcohol trap contained about 5 ml. of acetic acid with a blue layer on top. All of these materials were combined, made alkaline with sodium hydroxide, and steam distilled. The distillation was continued until about 150 ml. of water was collected along with the distilled organic compounds. The distillate was extracted with petroleum ether and the water discarded. The blue petroleum ether solution was washed with eighty-five per cent phosphoric acid, which removed the blue color. The phosphoric acid was washed with petroleum ether and this wash was combined with the petroleum ether previously used.

The phosphoric acid was diluted with water and extracted with petroleum ether. This blue petroleum ether extract was dried over calcium sulfate and chromatographed through alumina; and the solvent was evaporated under carbon dioxide. About 0.1 g. of blue oil was present. To this blue oil was added 0.12 g. of 1,3,5-trinitrobenzene and the mixture was just dissolved in hot ethyl alcohol (3 ml.). On cooling black needles separated which after three recrystallizations from ethyl alcohol melted at 145-151°.

Further recrystallization was not possible due to the lack of sufficient material. The melting point of the product first separated was 121-131°.

The petroleum ether solution which had been freed of the blue azulene was evaporated and 1 g. of product was obtained. This product was then distilled and two main fractions were collected One fraction boiled at 255-265° and the larger fraction boiled at 280-285°. The temperatures are those of the bath liquid around the small distillation flask. The bath temperature was raised slowly and carefully so that every opportunity was given the liquid in the flask to acquire the same temperature as the bath. There was a little tarry residue. The material distilling at 280-285° weighed 0.47 g. It was allowed to react with 0.69 g. of styphnic acid, ten per cent in excess of the theoretical amount, in alcohol. The material crystallized as a golden yellow compound when there was only a small amount of solvent present. It was considerably more soluble than styphnic acid. If the solvent was cooled in Dry ice-alcohol, after crystallization more solvent could be added to wash the compound. Melting points of the compound were as follows: first crystallization, m.p. 97-105°; second crystallization, m.p. 115-118°; third crystallization, m.p. 118-121°; fourth crystallization, m.p. 120-121.5°. Lack of material hampered further work on this compound.

The alkali soluble residue left in the flask after steam distillation was acidified and extracted with benzene. About 2 g. of red oil was present after evaporation of the benzene. This oil was dissolved in alkali, dimethyl sulfate was added, and the mixture shaken for one hour. After three days the solution was made alkaline

again and the excess methyl sulfate destroyed by warming. The brown oil was extracted with ether, and the ether evaporated. The residue was dissolved in petroleum ether, the petroleum ether washed with water and then dried over calcium sulfate. After chromatographing through alumina, a yellow oil remained on evaporation of the solvent. The yellow oil gave a flocculent precipitate on dissolving in alcohol and cooling. (The oil did not crystallize on cooling without adding a solvent.) The precipitate formed in alcohol melted and dissolved on warming to room temperature.

Dehydrogenation of Pyrethrosin with Sulfur

15 g. of pyrethrosin and 3.2 g. of sulfur were well mixed and the mixture heated to 250°. The heating was discontinued after two hours since no liquid reflux was observed and since the mixture had rapidly polymerized to a black solid. The reaction flask, which was heated in a metal bath, had an air cooled condenser joined to it. The first hour of heating was done under a pressure of 30 mm., but the vacuum had to be released because of the frothing that occurred when the acetic acid came off. After another hour of heating the experiment was given up.

Dehydrogenation of Pyrethrosin with Selenium

30 g. of pyrethrosin was thoroughly mixed with 40 g. of selenium. The mixture was heated under an air cooled condenser in a metal bath. The bath temperature was 300° ± 10 and the duration of heating was 36 hours. Hydrogen selenide could be readily detected at the top of the condenser. During the reaction a brown glassy resin formed in the flask and there was some reflux from the condenser.

The mixture was then distilled from the reaction flask by replacing the air condenser with a distillation head. The distillation was done at atmospheric pressure employing a free Bunsen flame. The flask was heated until no more distillate was obtained.

The brown oil which was obtained from this distillation was then placed in the distillation pot under an efficient column and redistilled. Four fractions were collected at a pressure of 30 mm.: first fraction, boiling at 94-128°, 0.5 ml., n_D^{25} = 1.4896, light yellow liquid; second fraction, boiling at 128-155°, 1.0 ml., n_D^{25} = 1.4953, colorless liquid; third fraction, boiling at 155-180°, 1.5 ml., blue liquid; fourth fraction, boiling at 180-215°, 1.5 ml., blue-black liquid. The first fraction when treated with picric acid showed a slight coloration, but no picrate separated when it was treated with an alcoholic solution of picric acid. The second fraction formed a picrate when an alcoholic solution of picric acid was added and the mixture cooled. The picrate was filtered and dried. It was then dissolved in benzene and petroleum ether and passed thru a column of alumina. The solvent was evaporated and picric acid in alcohol was added. The picrate obtained melted 102-108°. Further crystallization was not possible due to the small amount of compound available. The third and fourth fractions were combined and the azulene removed with eighty-five per cent phosphoric acid. The azulene-free material did not form a picrate with picric acid in alcohol. The phosphoric acid was diluted and the azulene was extracted with petroleum ether. The solvent was evaporated and 1,3,5-trinitrobenzene in alcohol was added to the blue oil.

The trinitrobenzenate was filtered, dried, and dissolved in petroleum ether. After passage through a column of alumina, the solvent was removed and the blue oil was again treated with 1,3,5-trinitrobenzene in alcohol. The trinitrobenzenate melted at 143-148°.

Dehydrogenation of Pyrethrosin with Nickel on Kieselguhr and Benzene

The method of Adkins (11) was employed to dehydrogenate pyrethrosin. 5.0 g. of pyrethrosin, 45 ml. of thiophene-free benzene, and 5 g. of nickel on kieselguhr was heated to 300° in a bomb for four hours. The catalyst was centrifuged from the benzene, washed with ethyl acetate and centrifuged again. The benzene-ethyl acetate mixture was evaporated in a stream of carbon dioxide. This material was very soluble in ethyl acetate and chloroform and insoluble in petroleum ether. Since it was not possible to crystallize the compound, purification was attempted by throwing out the compound from ethyl acetate solution with petroleum ether. After repeating this procedure several times and centrifuging the precipitate, crystallization of the compound was tried from ethyl alcohol and from a chloroform-petroleum ether mixture without success.

Hydrogenation of Pyrethrosin with Copper-Chromium Oxide

30 g. of pyrethrosin, 200 ml. of pure dry dioxane, and 10 g. of copper-chromium oxide catalyst (12) were placed in a hydrogenation bomb. This mixture was hydrogenated at 300° at a pressure of 7000 pounds per square inch of hydrogen for four hours.

The material found on opening the bomb was colorless and soluble in dioxane. The bomb was rinsed with pure dioxane and the catalyst which was still black was centrifuged off. The dioxane solution was distilled through a short fractionating column. The following fractions were obtained: boiling at 86-87.5°, 5 ml.; 87.5-91°, 50 ml; 91-99°, 100 ml; and 99-101.5°, 150 ml.. An iodoform test was tried on the dioxane which came from the bomb and a yellow precipitate of iodoform, m.p. 119-121°, was obtained. The fraction, boiling at 86-87.5°, was dried over potassium carbonate and 3 ml. of it was treated with 0.5 g. of 3,5-dinitrobenzoyl chloride. The melting point of the 3,5-dinitrobenzoate obtained was 92.0-92.5°, literature value of ethyl ester 92°, mixed melting point with known ethyl ester was 92-93°.

This fraction, boiling from 86-87.5°, was tested for methyl alcohol with hot copper gauze. When heated very hot the gauze was reduced, but no odor of formaldehyde was detected. A comparison with known methyl alcohol indicated the probable absence of methyl alcohol in the dioxane solution.

After removing the last of the dioxane with a water pump, the material remaining was a rather viscous liquid of a light yellow color. By distillation at 1 mm. pressure 3-4 ml. of a forerun, boiling from 60 to 80° (I), was obtained.

2.134 mg. of compound gave 6.564 mg. of carbon dioxide and 2.535 mg. of water.

C = 83.94% H = 13.55%

14.6 g. of a fraction, boiling from 115 to 130° (II), was obtained. From the variation in viscosity of this fraction it seemed that there were two different compounds present.

3.760 mg. of sample gave 11.079 mg. of carbon dioxide and 4.377 mg. of water.

C = 80.41% H = 13.03%

Calculated for $C_{15}H_{28}O$

C = 80.26% H = 12.53%

Hydrogenation of Oxygen-containing Compound (II) Obtained by Hydrogenation of Pyrethrosin

14.6 g. of (II) was dissolved in 150 ml. of pure dioxane and hydrogenated for seven hours at 330° and 7000 pounds of hydrogen with 10 g. of copper-chromium oxide (12) catalyst. The bomb was rinsed out with dioxane and the catalyst was centrifuged off. The material left, after distilling the dioxane, boiled at 81-90°/1 mm.. 10 g. of this colorless liquid (I) was obtained. Redistillation from a small column at atmospheric pressure yielded 8 g. of (I) boiling at 256-270°.

Dehydrogenation of compound (I) by Adkin's method (11)

8. g. of compound (I), 5 g. of nickel on Kieselguhr, 45 ml. of pure benzene, and 1000 pounds pressure of nitrogen were placed in a small bomb and heated to 350° for twelve hours.

The material from the bomb had a slight blue fluorescence. It was washed out with benzene and the catalyst centrifuged and the benzene distilled. 8.3 g. of material remained which was distilled under vacuum. There was a forerun of 1 g. boiling at 30-65°/50 mm..

The main fraction boiled at 103-107°/ 5 mm. 7 g. of material boiling in that range was isolated. The refractive index was $n_D^{32} = 1.4685$. Tetranitromethane gave a golden yellow color with the compound. The compound was insoluble in concentrated sulfuric acid, water, ten per cent sodium hydroxide, fuming sulfuric acid, and dimethyl sulfate. At 19 mm. the compound distilled at 134-139°.

3.699 mg. of sample gave 11.512 mg. of carbon dioxide and 4.261 mg. of water.

C = 84.90% H = 12.89%

3.585 mg. of sample gave 11.120 mg. of carbon dioxide and 4.213 mg. of water.

C = 84.60% H = 13.15%

These analyses were run by weighing the compound in an open boat and transferring the boat rapidly to the combustion tube. They are probably low for this reason.

Dehydrogenation of compound (I) with palladium on charcoal

The catalyst for this dehydrogenation was prepared according to Linstead (13) after the method of Willstaetter and Waldschmidt-Leitz (14). For use in this experiment it was mixed with an equal weight of asbestos washed with nitric acid.

This experiment was a vapor phase dehydrogenation according to the method of Linstead (9).

3.85 g. (4.5 ml.) of the compound was added at the rate of 1 drop every ten minutes to the catalyst tube heated to 330°. When all the compound had been added, the tube was swept out with

nitrogen. The volume of the gas collected was read just prior to the sweeping process. After the first pass 315 ml. of gas had been collected and 3.45 g. of a compound whose refractive index was $n_D^{25} = 1.477$. The catalyst was removed and replaced with fresh catalyst. The 3.45 g. of compound from the first pass was added at the same rate to the fresh catalyst at 350°. This second pass produced 490 ml. of gas and 2.85 g. of liquid with an index of $n_D^{25} = 1.4946$. The liquid recovered from the second pass was added at the same rate to fresh catalyst at 350°. This time 235 ml. of gas was formed and 2.28 g. of product recovered with an index of $n_D^{25} = 1.5027$. A fourth pass of liquid, at 350°, produced 110 ml. of gas and 1.82 g. of product with an index of $n_D^{25} = 1.5060$.

Following the fourth pass, several ml. of cyclohexane, at 330°, was run through the old catalyst fairly rapidly. About one-fourth of the theoretical yield of gas came off immediately, indicating that the catalyst was active.

The test for unsaturation with tetranitromethane was positive. A layer of hydrocarbon 16 mm. deep was shaken with 38 mm. of dimethyl sulfate in a capillary tube. The hydrocarbon layer remaining was only 9 mm. deep. The 1.82 g. of hydrocarbon was shaken with 6 ml. of dimethyl sulfate and the two layers separated. The dimethyl sulfate insoluble layer had an index $n_D^{25} = 1.4786$. The dimethyl sulfate-hydrocarbon layer was treated with 8.4 g. of potassium hydroxide in 16 ml. of water. After hydrolysis of the dimethyl sulfate more water was added to dissolve the potassium methyl sulfate or potassium sulfate and a yellow oil came to the

surface of the water. The oil was extracted with petroleum ether and the petroleum ether solution was washed with water and dried over calcium sulfate. After passing the solution through alumina, the solvent was evaporated leaving a liquid with an index of $n_D^{25} = 1.5354$.

4.734 mg. of sample gave 15.495 mg. of carbon dioxide and 4.318 mg. of water.

C = 89.32% H = 10.21%

3.209 mg. of sample gave 10.480 mg. of carbon dioxide and2.842 mg. of water.

C = 89.12% H = 9.91%

3.088 mg. of sample gave 10.148 mg of carbon dioxide and 2.866 mg. of water.

C = 89.68% H = 10.39%

When a few drops of the unsaturated hydrocarbon was added to a picric acid solution in alcohol, an orange color formed. When this orange solution was cooled to 5° in the ice box, orange needles formed which when dried melted at 109-112°. The picrate was not pure since crystals of picric acid could be distinguished.

10 drops of the unsaturated hydrocarbon was added to 0.2 g. of styphnic acid in absolute alcohol. The mixture turned a darker yellow on addition of the hydrocarbon. After standing in the ice box for several days yellow crystals formed. These crystals when sucked dry lost their yellow-orange color and melted at 176-177° (m.p. of styphnic acid). The orange colored filtrate when cooled and stirred became glassy, but did not crystallize. The orange oil was dissolved in alcohol and cooled in dry-ice-alcohol. The orange solution did not crystallize.

To 0.2 g. of 1,3,5-trinitrobenzene was added 7 drops of unsaturated hydrocarbon. Absolute alcohol was added several drops at a time until the mixture just dissolved in the warm alcohol. Yellow crystals separated on cooling which melted at 96-99° with preliminary sintering. These crystals were then dissolved in alcohol and recrystallized. The crystals then which first separated melted at 105-107°. The crystals found in the mother liquor melted at 85-90°. Both sets of crystals were recombined and recrystallized from an almost saturated solution of 1,3,5-trinitrobenzene. The crystals so obtained melted at 105-115° and the crystal shapes were not homogeneous, some being plates and others needles. The crystals melting at 105-115° were extracted with absolute alcohol in the cold. The fairly insoluble white plates which remained were apparently trinitrobenzene for they melted at 123-123.5°. After concentration of the alcohol, yellow needles melting at 84-95° were obtained. Another extraction and evaporation yielded crystals melting at 111-116°.

The unsaturated hydrocarbon (3 drops) was shaken with 12 drops of concentrated sulfuric acid, with which it formed an emulsion. To this emulsion was added 12 drops of concentrated nitric acid drop by drop with shaking. The solution formed a dark red-brown oil on top of the acids. This oil was poured into cold water and filtered. An amorphous yellow compound was present. It was taken up in alcohol and cooled. Crystals did not form, but the same yellow amorphous product was obtained again.

Products of the Hydrogenation of Pyrethrosin with Copper-Chromium Oxide

75 g. of pyrethrosin in 500 ml. of pure dioxane was hydrogenated at 300° and 7000 pounds pressure of hydrogen using 25 g. of copper-chromium oxide (12). The time of hydrogenation was six hours. After removing the material from the bomb, the catalyst was filtered off, and the dioxane was distilled from the hydrogenated product. The product was distilled through a modified Widmer column and the following fractions collected at 2 mm.: 4.3 g., boiling from 53-100° (principally 60-80°); 22.1 g., boiling from 111-140° (principally 125-130°); 10.7 g., boiling from 140-180°; 5.9 g., residue. The total weight of product was 43.0 g.. Theoretical yield of product for loss of 4 oxygen and 2 carbon atoms during hydrogenation was 53 g..

An analysis was run on the glass (III) which boiled at 140-80°/2 mm.

5.944 mg. of sample gave 16.279 mg. of carbon dioxide and 6.049 mg. of water.

C* = 74.75% H = 11.36%

Calculated for $C_{15}H_{28}O_2$

C = 74.95% H = 11.74%

The Hydrocarbon (I) Boiling at 60-80°/1 mm.

In distilling the products of one of the hydrogenations of pyrethrosin with copper-chromium oxide two layers separated and the distillation of the hydrocarbon (I) was cut almost as soon as it had started to come over. The bottom layer turned out to be ethylene

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* The author is indebted to Mr. P. J. Wingate for this analysis.

glycol from the hydrogenation of the dioxane. The top layer was the best cut of hydrocarbon (I) ever obtained from distillation of hydrogenated pyrethrosin for it analyzed for almost pure hydrocarbon.

3.537 mg. of sample gave 11.126 mg. of carbon dioxide and 4.300 mg. of water.

C = 85.84% H = 13.60%

Calculated for $C_{15}H_{28}$

C = 86.46% H = 13.54%

Distillation of the rest (15 ml.) of the hydrocarbon (I) fraction at atmospheric pressure through a one foot Vigreux column yielded the following fractions.

TABLE II

Distillation of the Hydrocarbon (I) at Atmospheric Pressure

Temperature (°C.)	Approximate Amount (ml.)
244-58	2.0
259-62	2.0
262-65	3.0
265-68	2.5
268-71	2.0
271-74	1.5
274-77	1.0
277-80	1.0

The fraction of (I) boiling at 262-265° was analyzed.

6.487 mg.of sample gave 20.133 mg. of carbon dioxide and 7.530 mg. of water.

C = 84.70% H = 12.99%

4.578 mg. of sample gave 14.201 mg. of carbon dioxide and 5.477 mg. of water.

C = 84.65% H = 13.31%

The rotation of the hydrocarbon fraction (I) taken in a one decimeter tube at room temperature was 1.01 degrees to the right.

The Alcohol (II) Boiling at 120-130°/ 1 mm..

Analyses run on (II) from one of the copper-chromium oxide hydrogenations of pyrethrosin indicated that it probably consisted of monohydroxy alcohols.

3.206 mg. of sample gave 9.401 mg. of carbon dioxide and 3.715 mg. of water.

C = 80.02% H = 12.97%

4.764 mg. of sample gave 13.867 mg. of carbon dioxide and 4.932 mg. of water.

C = 79.43% H = 11.58%

The second analysis was on the more viscous material present in this fraction.

Active hydrogen determinations were run on (II) from a hydrogenation of a large quantity of pyrethrosin and on (II) from a small hydrogenation run. The former gave 0.92 equivalents of active hydrogen and 0.09 equivalents of carbonyl groups for (II). The latter gave 0.91 equivalents of active hydrogen and 0.17 equivalents of carbonyl groups for (II). The calculation of these values was based on a molecular weight of 235.

The fraction (II) in a one decimeter tube at room temperature rotated the plane of polarization 2.70 degrees to the right.

Attempts to make functional derivatives

1.g. of 3,5-dinitrobenzoyl chloride and 0.5 g. of (II) were refluxed for two hours in 5 ml. of pyridine. On working up the product, no crystals were obtained.

Phenylisothiocyanate was warmed on the steam bath overnight with (II), but it did not yield anything crystalline.

Phenylisocyanate was heated on the steam bath with (II) for three hours. On cooling in Dry ice-alcohol and adding a little petroleum ether, a gray solid was obtained which sintered at 122° and was melted (over a wide range) at 230°.

Reaction of Alcohol (II) with Hydrobromic Acid

5 g. of (II) was added to 25 ml. of constant boiling hydrobromic acid and refluxed for four hours. This mixture was diluted with water and ether was used to extract the organic material. The ether solution was washed with water and dried over calcium chloride. After distillation of the ether, the residue was distilled at atmospheric pressure. A few drops of red liquid distilled below 250° along with some hydrogen bromide gas. About 1 ml. of distillate was collected in the range 270-285° and 2.5° ml. at 285-295°. Very little residue was left. The liquid appeared water white until it came into contact with the air; then it turned a bright red, which deepened on standing. At the end of the distillation the drops which collected on the thermometer and fell back into the flask were blue colored.

The red liquid was insoluble in aqueous silver nitrate and gave only a slight precipitate of silver bromide on vigorous shaking of the mixture. The red liquid was soluble in alcohol and gave an almost colorless solution. When alcoholic silver nitrate was added, a copious precipitate of silver bromide was obtained. The refractive index of the red liquid was $n_D = 1.490$.

Nitric Acid Oxidation of Alcohol (II)

The experimental conditions were copied after those of Organic Syntheses for the preparation of adipic acid from cyclohexanol (15). 10 g. of (II) and o.1 g. of ammonium vanadate, were stirred and heated to 95-105°. To this mixture 42 g. of fifty per cent nitric acid was added over a period of twenty minutes and the heating was continued at the same temperature for two hours.

The thick gum found in the flask after cooling was extracted with ether and the ether solution was in turn extracted with dilute sodium hydroxide. Following the extraction of the acids, the ether was distilled; and the gum which remained was allowed to react with 2,4-dinitrophenylhydrazine in an alcoholic solution. On cooling of this alcohol solution, an amorphous red hydrazone separated and was filtered. After taking the hydrazone up in alcohol and cooling, the 2,4-dinitrophenylhydrazone was obtained in an amorphous form again. It melted at 60-95° and at 135-145° decomposition as evidenced by evolution of gas occurred. Further attempts at purification by crystallization from alcohol were unsuccessful.

The sodium hydroxide solution containing the acid fraction was acidified and extracted with ether. After removal of the ether, a gum remained which could not be induced to crystallize.

Chromic Acid Oxidation of Alcohol (II)

5.0 g. of (II) was dissolved in 25 ml. of glacial acetic acid and 3.0 g. of chromic acid was added and the mixture shaken. The reaction mixture soon warmed up enough to reflux the acetic acid. After refluxing the acetic acid mixture for ten minutes following the initial reaction, the mixture was poured into 500 ml. of water and made alkaline. The alkaline mixture was then steam distilled and 1000 ml. of water was collected which had a few drops of oil on the surface. This oil (IV) was extracted with 1 liter of ether in small portions and the ether evaporated. There remained 2.2 g. of almost colorless oil.

2,4-Dinitrophenylhydrazone of the oil (IV)

1.0 g. of (IV) was treated with 0.85 g. of 2,4-dinitrophenylhydrazine contained in a solution of 1.5 ml. concentrated hydrochloric acid and 75 ml. of alcohol. After refluxing the mixture for ten minutes, a yellow precipitate was formed on cooling which weighed 0.53 g.

After three recrystallizations from alcohol the hydrazone melted at 139-147°. It was then dissolved in petroleum ether and adsorbed on Brockmann's alumina. There appeared two layers in the column. The material which was adsorbed most firmly was dark orange and only a small band was present. When cut out and dissolved in alcohol, this orange material would not crystallize. The larger band at the bottom was yellow, and when developed with more petroleum ether, spread out; but did not show any more bands. This yellow band was extracted with and crystallized from alcohol. The product melted at 150-156°. The chromatographing and crystallization was repeated and the yellow shiny plates obtained melted at 153-163°.

Molecular weights determined using borneol as solvent were 395 and 411. Calculated for $C_{21}H_{30}N_4O_4$ was 402.

4.898 mg. of sample gave 11.157 mg. of carbon dioxide and 3.325 mg. of water.

C = 62.16% H = 7.59%

3.914 mg. of sample gave 8.874 mg. of carbon dioxide and 2.547 mg. of water.

C = 61.87% H = 7.28%

4.857 mg. of sample gave 11.129 mg. of carbon dioxide and 3.264 mg. of water.

C = 62.53% H = 7.52%

Calculated for $C_{21}H_{30}N_4O_4$

C = 62.6% H = 7.45%

Semicarbazide of oil (IV)

1.0 g. of (IV), 0.5 g. of semicarbazide hydrochloride, and 0.75 g. of sodium acetate were warmed in a solution of 40 ml. of alcohol. After cooling the mixture, a milky oil separated which failed to crystallize.

Dehydrogenation of Alcohol (II)

Liquid phase dehydrogenation of (II)

5.0 g. of (II) and 1.0 g. of palladium on charcoal (13) (the same catalyst as described on page 17) were heated at 260° in the liquid phase for fifteen hours. The rate of evolution of gas was about 1ml./15 sec. during the first few hours and it fell to 1 ml./ 12 minutes during the fifteenth hour.

The product was extracted from the catalyst with petroleum ether, transferred to another flask, and steam distilled. 1.27 g. of water-white liquid with a refractive index of n_D = 1.480 was obtained. This liquid was allowed to react with 1,3,5-trinitrobenzene in alcohol solution. The melting point of the golden benzenate from this reaction was 135.5-136° after it had been recrystallized five times from alcohol.

4.452 mg. of sample gave 9.678 mg. of carbon dioxide and 2.007 mg. of water.

C = 59.32% H = 5.04%

4.563 mg. of sample gave 9.965 mg. of carbon dioxide and 1.748 mg. of water.

C = 59.60% H = 4.29%

Calculated for $C_{19}H_{17}N_3O_6$

C = 59.5% H = 4.47%

Vapor phase dehydrogenation of (II)

5.7 g. of (II) was passed over palladium on charcoal (9) (the same catalyst as described on page 17) mixed with asbestos at 325°. (II) was added to the catalyst tube over a period of four hours and 1400 ml. of gas came off in this time. A second pass

with the same catalyst at 350° produced almost no gas. A third pass with the same catalyst above 380° produced only 250 ml. of gas; a blue color developed in the product from the third pass.

The azulene was extracted with eighty-five per cent phosphoric acid. The liquid remaining was washed with water and dried. Its index was $n_D^{21.5} = 1.4990$. This liquid was allowed to react with picric acid in alcohol. The dark red picrate melted at 179-180° after four recrystallizations from alcohol.

3.524 mg. of sample gave 7.562 mg. of carbon dioxide and 1.373 mg. of water.

C = 58.56% H = 4.36%

6.115 mg. of sample gave 12.983 mg. of carbon dioxide and 2.109 mg. of water.

C = 57.96% H = 3.86%

Calculated for $C_{20}H_{19}N_3O_7$

C = 58.2% H = 4.64%

The azulene was freed from the phosphoric acid by dilution with water and extraction with petroleum ether. After removal of the petroleum ether, the azulene was allowed to react with 1,3,5-trinitrobenzene in alcohol. Black, well-formed needles were isolatedwhich after three recrystallisations melted at 131-133°.

Dehydration of Alcohol (II) over Alumina

5.0 ml. of alcohol (II) was passed over activated alumina at 300°. After twelve hours, 4-5 ml. of a blue-green liquid (n_D = 1.483) was obtained. The dehydrated compound gave a positive test with tetranitromethane. When bromine in carbon tetrachloride was added to a solution of the compound in chloroform, the bromine was at first decolorized, and then immediately a purple color appeared in the solution. The purple deepened on adding more bromine. This test is one for azulene-producing compounds. (16)

The dehydrated compound was passed through a column of Brockmann's alumina with petroleum ether solvent. The dehydrated compound was then distilled at atmospheric pressure and the following fractions collected: boiling at 257-262°, 1.3 g.; boiling at 262-272°, 1.3 g.; boiling at 272-276°, 0.4 g.. Analyses on the fraction boiling at 262-272° indicated that it was not pure hydrocarbon.

2.541 mg. of sample gave 8.022 mg. of carbon dioxide and 2.816 mg. of water.

C = 86.15% H = 12.41%

3.791 mg. of sample gave 11.902 mg. of carbon dioxide and 4.185 mg. of water.

C = 85.68% H = 12.35%

All attempts to make crystalline hydrochlorides of these compounds were unsuccessful.

This dehydrated product was passed over old palladium on charcoal catalyst in the vapor phase. Very little hydrogen was evolved and although the dehydrogenated product did develop color when a solution of picric acid was added, no picrate could be isolated. Cyclohexane would not dehydrogenate with this catalyst, however.

Dehydrogenation of the dehydrated product with selenium at 300° produced no picrate-forming fraction and no azulene.

Repeated distillation of the dehydrated product through an efficient fractionating column at 30 mm. pressure separated the following fractions.

TABLE III

Fractions Isolated from Dehydrated Alcohol

by Distillation at 30 mm. Pressure

Temperature Range (°C.)	Refractive Index (n_D^{25})
113-131	1.4714
131-138	1.4769
138-142	1.4816
142-145	1.4845
145-148	1.4875
Residue	1.4938

An analysis on the fraction boiling at 138-142° indicated that even after repeated fractional distillation there was no pure hydrocarbon present in this fraction.

25.89 mg. of sample gave 81.63 mg. of carbon dioxide and 28.03 mg. of water.

C*= 86.5% H = 12.1%

Hydrogenation of Dehydrated Alcohol (II)

5.0 g. of dehydrated (II) boiling at 138-148° at 30 mm. was reduced with one-half teaspoon of Raney nickel catalyst in 50 ml. of absolute alcohol. The temperature of the hydrogenation was 100°,

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* The author is indebted to Mr. D. Kaufman for this analysis.

the pressure was 1400 pounds per square inch and the length of reaction was three hours.

After removal of the alcohol and catalyst, the product was twice distilled through an efficient fractionating column and the following fractions were isolated.

TABLE IV

Fractions Isolated from Hydrogenation of Dehydrated Alcohol (II) by Distillation at 30 mm. Pressure

Temperature Range (°C.)	Refractive Index (n_D^{25})
138-139	1.4705
142-143	1.4721
143-145	1.4739
145-146	1.4747
146-147	1.4752
Residue	1.4773

An analysis of the fraction boiling at 145-146° indicated that this fraction was nearly pure hydrocarbon.

14.88 mg. of sample gave 47.07 mg. of carbon dioxide and 17.56 mg. of water.

C* = 86.3% H = 13.2%

Calculated for $C_{15}H_{28}$

C = 86.46% H = 13.54%

The density of the fractions boiling at 138-143° was $d^{25} = 0.8721$. The density of the fractions boiling at 145-147° was $d^{25} = 0.8810$.

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* The author is indebted to Mr. D. Kaufman for this analysis.

Hydrogenation Experiments

Hydrogenation of pyrethrosin with copper-chromium oxide at 4000 pounds per square inch of hydrogen

10.0 g. of pyrethrosin, 5.0 g. of copper-chromium oxide (12) and 50 ml. of pure dioxane were shaken in a bomb at 250° and 4000 pounds per square inch of hydrogen for ten hours. After removal of the catalyst and solvent, the clear residue was distilled at 1 mm.. About half of the product distilled at 125-145°/ 1 mm.. The other half was viscous residue; it was not distilled.

Hydrogenation of glass (III) obtained from a previous copper-chromium oxide hydrogenation.

10.0 g. of glass (III) obtained in the hydrogenation described on page 21 was rehydrogenated in 45 ml of dioxane with 5.0 g. of copper-chromium oxide (12). The same conditions were used as in the original hydrogenation (300° temperature and 7000 pounds pressure of hydrogen for six hours). Upon working up the product the following fractions were obtained: boiling below 110°/ 1 mm., 0.3 g.; boiling at 125-145°/ 1 mm., 3.0 g.; boiling at 150-170°/ 1 mm., 2.0 g.; residue, 3.0 g..

Vigorous hydrogenation of pyrethrosin with Raney nickel

37.5 g. of pyrethrosin, 1.5 tablespoons of Raney nickel, and 500 ml. of absolute alcohol were shaken in a bomb for eight hours at 175° under 3000 pounds pressure of hydrogen. After removal of the catalyst and solvent, the straw-yellow, viscous product was distilled. 28.0 g. of product, boiling at 188-240°/ 2 mm., was collected. The material distilled without decomposition.

DISCUSSION

Isolation of Pyrethrosin

The principal difference between Schechter's method of isolation (8) and the method described was that he washed the crude material with low boiling petroleum ether in order to remove the gum. This step was found to be unnecessary since pyrethrosin could be obtained just as pure and just as easily without this step. Schechter removed the main body of insoluble impurities by allowing them to settle out in tall cylinders and decanting the supernatant liquid. This method required that the cylinders be kept at 72° during the hour of settling to prevent crystallization. The filtration through glass wool which replaced this settling process requires that the glass wool layer be not too thick; otherwise the time of filtration will be so long as to cause crystallization of the pyrethrosin during filtration. Schechter used charcoal to obtain easy filtration. Filter-Cel was successfully substituted for the charcoal, and the charcoal treatment was reserved for the second crystallization, where it removed the little color found in the first crystallization product.

The solubility of pyrethrosin in hot benzene was found useful whenever a non polar solvent must be employed for a reaction.

Dehydrogenation of Pyrethrosin with Palladium on Charcoal

Palladium catalysts are usually very satisfactory for dehydrogenation because the reaction can be conducted at moderate to high temperatures without too many side reactions (17). The trouble with any dehydrogenation of pyrethrosin itself is that the pyrethrosin decomposes at any temperature high enough for dehydrogenation to occur;

the major loss of material is a drawback.

The strange part about the results of the palladium dehydrogenations is that apparently no aromatic acid was isolated, and that very little phenolic fraction was present. Considering the large amount of oxygen present in pyrethrosin, more aromatic oxygen compounds would be expected, expecially using catalytic methods. That no more is obtained causes one to suspect that there is very little straightforward dehydrogenation taking place.

The analysis on the hydrocarbon separated as a picrate was intended only to show whether an aromatic hydrocarbon was present or not. The analysis was probably high in hydrogen from traces of moisture which may have been present in the potassium chlorate used in combustion. The values for the analysis lay roughly between the values for $C_{12}H_{12}$ and $C_{15}H_{18}$.

It was unfortunate that the azulene 1,3,5-trinitrobenzenate could not be purified to be compared with the azulene isolated by Haller and Schechter from a zinc dust pyrolysis of pyrethrosin. They describe that azulene as a 2,4,8-trimethylazulene (6). Since the azulenes can rearrange to naphthalene derivatives at 300° (18), the corresponding trimethylnaphthalene should be present in the dehydrogenation mixture. However, the only naphthalene compound tentatively identified was 1-methyl-7-isopropylnaphthalene, isolated as a styphnate. Since styphnates are generally satisfactory for mixed melting points, the styphnate obtained should be checked with known styphnate. Lack of material prevented carbon and hydrogen analysis on this styphnate.

Dehydrogenation with Selenium and by Adkins' Method

The experiment employing selenium should be repeated on a larger scale and the picrate and azulene 1,3,5-trinitrobenzenate obtained ought to be capable of purification, if obtained in larger quantities. It is interesting that almost no azulene was obtained until the final distillation at high temperature. This behavior probably means that the azulene is only formed by considerable rearrangement of the pyrethrosin skeleton.

The dehydrogenation by Adkins' method (11) undoubtedly changed the pyrethrosin in some manner, but it is likely that very little dehydrogenation occurred. This might be expected when dealing with a highly oxygenated compound like pyrethrosin. Surely any loss of oxygen as water would impair the activity of the nickel catalyst in a benzene solution. At least this observation is true of hydrogenations where separation of water is generally inimical to further reaction. The fact that Adkins was able to dehydrogenate compounds containing one oxygen might be looked upon as a refutation of this argument, however there is a great deal of difference between one oxygen in a compound and five oxygens.

Hydrogenation of Pyrethrosin

Hydrogenation of pyrethrosin was undertaken in order to stabilize the molecule and to prevent gross decomposition during subsequent dehydrogenations. The first aim was to hydrogenate pyrethrosin completely to the hydrocarbon and to dehydrogenate the hydrocarbon by catalytic means. The first part of this task was generally successful. Oxygen could be stripped from pyrethrosin by hydrogenation

and a large percentage of hydrocarbon obtained. Contrary to expectations and hopes, the hydrocarbon proved very resistant to dehydrogenation. Adkins' method (11) would not dehydrogenate the compound, and the starting product could be recovered. Dehydrogenation with palladium catalyst in the vapor phase should have dehydrogenated any hydrocarbon with a skeleton capable of aromatization. However, although some dehydrogenation did occur, and although naphthalenes or like compounds were found in the products of dehydrogenation, dehydrogenation was obviously not a favored reaction. The analyses on the resulting mixture as compared with the original hydrocarbon showed that more than three moles of hydrogen was liberated per molecule. This would indicate that the original compound was at least bicyclic. The difficulty of dehydrogenation was probably due to a five membered ring or some other system which would not dehydrogenate readily. Further work on this dehydrogenation should include a special investigation of the dehydrogenation product for compounds like p-cymene. Such compounds frequently escape detection because they do not form picrates or other addition complexes.

Products of the Hydrogenation of Pyrethrosin

Pyrethrosin is by nature not suited for isolation of anything, except a hydrocarbon, in a pure state by hydrogenation. The five oxygens present cause this difficulty as well as the formation of optical isomers by hydrogenation of the methylene group. The ester group should hydrogenate smoothly and give nearly one product, the corresponding alcohols. Ethyl alcohol could be identified

in the reaction products. The alcohol corresponding to pyrethrosin minus the acetyl group, however, has never been isolated nor have any of its derivatives been made. The secondary alcohol should not have changed; possibly under the drastic conditions employed it may have been reduced to hydrocarbon. The real trouble maker is the lactone group. It can hydrogenate to a cyclic ether, to an acid, to give two hydroxyl groups, and to hydrocarbons, or combinations and mixtures of these possibilities. It is no wonder then that purification of the 2,4-dinitrophenylhydrazone of the product of oxidation of this mixture is not readily accomplished if at all. There exists also, to make the situation more complex, the possibility of carbon to carbon cleavage during drastic hydrogenation.

Dehydrogenations of alcohols often occur more smoothly than those of many other types of compounds (19). This seems to be the case here. At least, a sharp melting 1,3,5-trinitrobenzenate and a sharp melting picrate of a naphthalene or naphthalenes have been obtained as well as a 1,3,5-trinitrobenzenate of an azulene. Unfortunately a search of the literature revealed no compound having below fifteen carbons corresponding with any of these compounds. Limited quantities of these products have hampered further investigations. A dimethylnaphthalene picrate listed in Beilstein melting at 180° does not compare to the melting point of any picrate of all the ten possible dimethylnaphthalenes. 1,6-dimethylnaphthalene has a trinitrobenzenate listed as melting at 134-135°, but its picrate melts at 112.5-113.5°.

It is rather strange that the dehydrated alcohol (II) did not dehydrogenate with selenium. Compounds having an unsaturation present should be particularly prone to dehydrogenate with one of the chemical dehydrogenating agents such as selenium. This observation must be considered as another demonstration of the reluctance of these compounds to dehydrogenate.

The only other way to attack the basic structure would be to prepare the pure hydrocarbon corresponding to pyrethrosin. A fairly pure hydrocarbon was obtained by dehydration and subsequent hydrogenation. However a lengthy series of fractional distillations was necessary and time unfortunately was lacking for a complete examination of the hydrocarbon.

The hydrocarbon obtained by hydrogenation should be purified and identified and compared to the hydrocarbon obtained by dehydration and subsequent hydrogenation of the alcohol (II). It would be interesting to see whether the two possessed the same ring structure.

The Skeleton of Pyrethrosin

The hydrocarbon corresponding to pyrethrosin probably has the formula, $C_{15}H_{28}$, and is a bicyclic compound. The most likely evidence for this statement is the 2,4-dinitrophenylhydrazone which corresponds to a $C_{15}H_{26}O$ ketone; and the one analysis on the hydrocarbon corresponding to $C_{15}H_{28}$. The analyses of the alcohol (II) roughly corresponded to $C_{15}H_{28}O$, but the material analyzed was obviously a mixture. The loss of more than three moles of hydrogen per mole of hydrocarbon on dehydrogenation is also indicative of a bicyclic system. The difficulty of dehydrogenating must be due to

some peculiar ring arrangement; such difficulty of dehydrogenation has been observed in the case of five-membered rings and in the case of substances possessing quaternary methyl groups. However, even quaternary methyl groups should be eliminated under the conditions of the vapor phase dehydrogenation. There may even be a quaternary methyl group present in addition to a peculiar ring system. Such is the case with α- and β-gurjunene. They are two tricyclic sesquiterpenes of the empirical formula, $C_{15}H_{24}$,(20), isolated from gurjun-balsam oil. If the gurjunene mixture is dehydrogenated with sulfur (21) or selenium in the liquid phase or with nickel (22) in the vapor phase an azulene $C_{15}H_{18}$ is obtained. By dehydrogenation with sulfur (21) neither of the two sesquiterpenes nor the products regenerated from their hydrochlorides yielded picrate-forming naphthalene compounds.

Another item of similarity between these compounds and the hydrogenated pyrethrosin compounds is that by heating α-gurjunene to 330° a mixture of azulenes (23) was formed. The $C_{15}H_{28}O$ alcohol from pyrethrosin formed some azulene, as evidenced by the blue color present, during its passage over alumina at 300°.

α- and β-gurjunene differ in their reaction with hydrochloric acid (24). α-gurjunene forms a hydrochloride smoothly; which by removal of the hydrogen chloride with alcoholic potassium hydroxide, and hydrogenation of the olefin gave the same saturated hydrocarbon, $C_{15}H_{26}$, as obtained by hydrogenation of α-gurjunene.

β-gurjunene does not form a hydrochloride; but isomerizes to iso-β-gurjunene which has been shown to be bicyclic by its hydrogenation to a $C_{15}H_{28}$ compound.

Treatment of α-gurjunene (24) with hot sulfuric acid-acetic acid mixture isomerized α-gurjunene to the bicyclic iso-α-gurjunene. Iso-α-gurjunene was identified as bicyclic by its hydrogenation to a compound, $C_{15}H_{28}$.

A remarkable comparison can be made between this tetrahydro-iso-α-gurjunene and the hydrocarbon $C_{15}H_{28}$, obtained by hydrogenation of of dehydrated $C_{15}H_{28}O$ alcohol (II) from pyrethrosin.

TABLE V

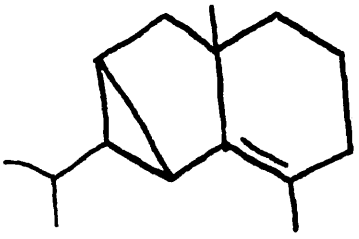
Comparison of Tetrahydro-iso-α-gurjunene

with the Hydrocarbon $C_{15}H_{28}$ from Pyrethrosin.

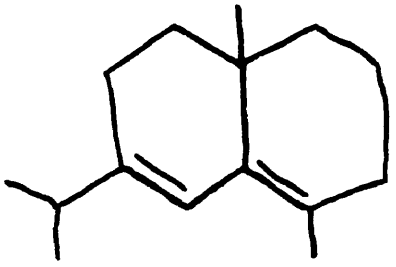
Tetrahydro-iso-α-gurjunene	$C_{15}H_{28}$ Hydrocarbon from Pyrethrosin
$d^{20} = 0.875$	$d^{25} = 0.876$ (Averaged Value)
$n_D = 1.4765$	$n_D^{25} = 1.4731$ (Averaged Value)

The structures of α-gurjunene and iso-α-gurjunene were established by Triebs (24) in 1935 through oxidative degradation.

α-gurjunene



Iso-α-gurjunene



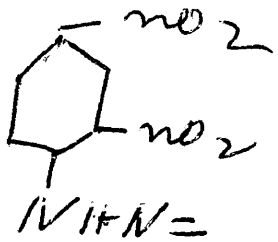
Another point of interest is that 1-methyl-7-isopropyl naphthalene would be expected from iso-α-gurjunene on dehydrogenation, as well as from any compound with the same carbon skeleton as iso-α-gurjunene.

The many similarities between α- and β -gurjunene and pyrethrosin compounds in chemical and physical properties cause one to wonder whether the carbon skeleton of pyrethrosin may not be like that of α-gurjunene or at least closely related to it.

Starting with $C_{17}H_{22}O_5$, the acetic acid can be accounted for leaving $C_{15}H_{20}O_4$ as the pyrethrosin alcohol. Besides the hydroxyl group of the ester linkage there is a secondary alcohol group (25). Replacing these hydroxyl groups with hydrogen would leave $C_{15}H_{20}O_2$. The two remaining oxygens are in the lactone ring (7). Replacing them with hydrogen would leave $C_{15}H_{24}$. The presence of one methylene group in pyrethrosin has been shown by Wingate (25). There has never been any evidence for more than one double bond in pyrethrosin. If the methylene group is hydrogenated, $C_{15}H_{26}$ would be the saturated skeleton of pyrethrosin. This empirical formula is the same as that of α-gurjunene. Drastic hydrogenation would be expected to open a three membered ring and would account for the $C_{15}H_{28}O$ alcohol. The possible relationship between this $C_{15}H_{28}O$ alcohol and iso-α-gurjunene has already been suggested. The alcohol group remaining after hydrogenation is most probably the secondary alcohol group originally present as such. There may be another secondary alcohol group tied up in the lactone which would account for the difficulty of preparing derivatives of the $C_{15}H_{28}O$ alcohol, if this other secondary alcohol were present as an impurity in the hydrogenation mixture. The glass (III) obtained in hydrogenation is probably the glycol having two secondary alcohol groups; it analyzes roughly for a dihydroxy bicyclic compound. The methylene group must be connected

$C_{21} H_{30} N_4 O_4$

$C_6 H_4 N_4 O_4$



MW =

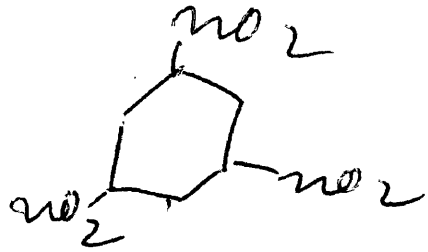
$C_6 H_4 N_4 O_4$

$C_{15} H_{26}$

$\therefore C_{15} H_{26} O$ fm. oxd. of alcohol

$C_{19} H_{17} N_3 O_6$

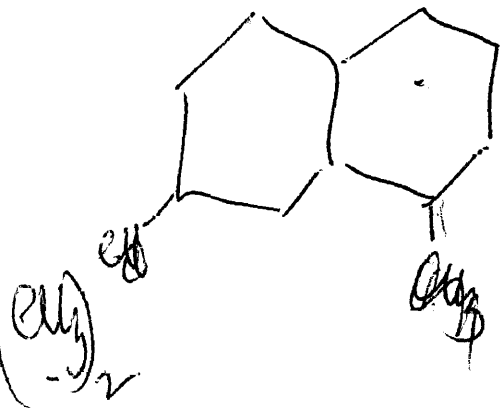
$C_6 H_3 N_3 O_6$



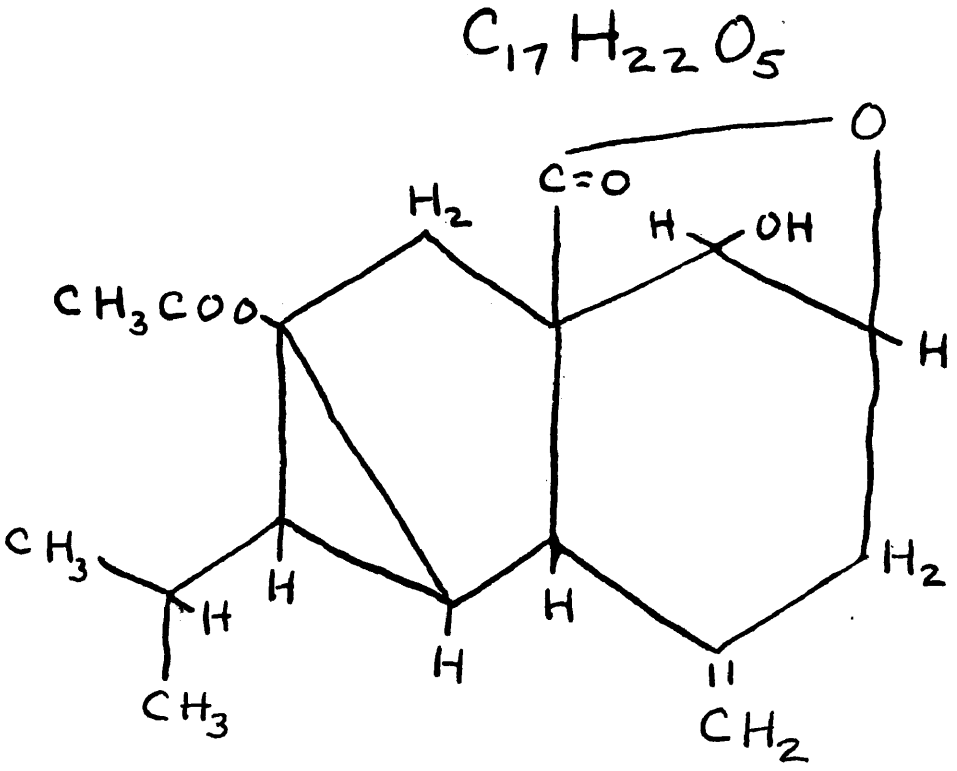
$C_6 H_3 N_3 O_6$

$C_{13} H_{14}$ fm. dehydrogen of alc.

diff. fm oxd. prod. $C_2 H_{12} O$



to a carbon holding no hydrogen; otherwise, there would be no isomers produced on hydrogenation of the double bond. The hydroxyl holding the acetyl group is probably tertiary; such a group would explain the ease with which acetic acid is lost. Pyrethrosin, then, may be postulated as possessing the following structure or a related one.



SUMMARY

1. Pyrethrosin has been dehydrogenated to yield a substance which forms a styphnate corresponding in melting point with that of 1-methyl-7-isopropylnaphthalene.
2. Hydrogenation of pyrethrosin yields an alcohol and a hydrocarbon fraction. The alcohol probably has the formula $C_{15}H_{28}O$.
3. Dehydrogenation of the alcohol, $C_{15}H_{28}O$, yielded a compound whose picrate melted at 179-180° and a compound whose trinitrobenzenate melted at 135.5-136°. These two compounds may or may not be related. An azulene trinitrobenzenate melting at 131-133° was also isolated.
4. A hydrocarbon, probably $C_{15}H_{28}$, has been obtained by dehydrating the $C_{15}H_{28}O$ alcohol and then hydrogenating the dehydration product.
5. The hydrogenation of pyrethrosin to hydrocarbon and an attempt to dehydrogenate the hydrocarbon formed have been described.
6. The isolation of pyrethrosin from still residues and its purification has been described.
7. A structure has been postulated for pyrethrosin. This structure possesses the carbon skeleton of α-gurjunene.

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