The carbinol was dehydrated by heating 10 g. (0.037 mole) under reflux in an oil-bath at 210–215° for fifteen minutes, cooling, adding 10 ml. of 20% sulfuric acid, refluxing one hour, and again cooling. Suction filtration of the crude product and crystallization from 85 ml. of 95% alcohol (with Norit) gave 8.1 g., 88%, melting 84–86°.[3]

A mixture of 5 g. (0.02 mole) of 1,1-di-(*p*-chlorophenyl)-ethylene, 80 ml. of absolute alcohol, and 0.15 g. of Adams platinum black catalyst was allowed to react with hydrogen at 35 pounds pressure in the Parr low-pressure hydrogenator for thirty minutes. The pressure drop corresponded to 0.02–0.03 mole of hydrogen consumed. After filtering and removal of the solvent the residue was crystallized from 90% acetic acid to give 3.1 g., 62% of the theoretical, melting 54–55°, boiling 143–145° at 1–2 mm. pressure. Neither the pure product nor its solutions showed any fluorescence in visible or ultraviolet light.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: Cl, 28.24; mol. wt., 251. Found: Cl, 28.18; mol. wt., 252.

When the time of hydrogenation was two hours, considerably more than the theoretical amount of hydrogen was consumed, the reaction mixture contained dissolved hydrogen chloride, and the yield of ethane was only 0.7 g. (14%). Apparently some hydrogenolysis of the chlorine atoms occurred.

Oxidation of 1.0 g. of the ethane by a solution of 40 ml. of glacial acetic acid containing 4 g. of chromic acid and four drops of sulfuric acid at reflux for two hours gave 0.9 g. of 4,4′-dichlorobenzophenone, melting 142–144°, which showed no depression in a mixed melting point with the authentic ketone. A mixed melting point of the ethane with authentic di-(*p*-chlorophenyl)-methane[4] (m. p. 54–55°) was 40–50°. A picrate derivative of the ethane did not form from the usual procedure.[8]

Reduction of Di-(*p*-chlorophenyl)-methylcarbinol.—A mixture of 13.4 g. (0.05 mole) of carbinol, 40 ml. of absolute alcohol and about 3 g. of nickel-on-kieselguhr (prepared from Harshaw Chemical Co. no. 78 catalyst, nickel carbonate on kieselguhr) was hydrogenated in an American Instrument high-pressure hydrogenator at 200–205° for 3.5 hours. The initial pressure at room temperature was 710 pounds, and the pressure drop of 540 pounds represented 0.1 mole of hydrogen. Isolation of the product as described before gave 1.8 g. of ethane, 14%, melting 54–55°. Undoubtedly this yield could be increased by further study of the hydrogenation conditions.

Acetaldehyde plus Chlorobenzene.—Eighty grams (0.6 mole) of anhydrous aluminum chloride was added to 150 ml. of chlorobenzene and the mixture saturated at 0° with anhydrous hydrogen chloride. Twenty-two grams (0.5 mole) of acetaldehyde dissolved in 50 ml. of chlorobenzene was added dropwise and with stirring during one hour, the temperature being held at 0–10° by an ice-bath. The reaction was continued for four hours at 50°, the product hydrolyzed in cold dilute hydrochloric acid and then steam distilled to remove excess chlorobenzene. The residue was dried and distilled to give 25 g. (20% yield calculated as di-(*p*-chlorophenyl)-ethane) at 160–170° and 6–7 mm. pressure. Redistillation gave 22 g., 167–168° (6–7 mm.) of a yellow oil showing a strong blue fluorescence; $n^{20}D$ 1.5918. Oxidation with chromic acid in acetic acid gave 4,4′-dichlorobenzophenone, m. p. 143–144°. Analysis showed that the chlorine content was slightly lower than that for di-(*p*-chlorophenyl)-ethane.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: Cl, 28.24. Found: Cl, 28.04, 28.05.

The substitution of 15% fuming sulfuric acid for aluminum chloride in a similar experiment gave only black, tarry products; 7.5 g. (0.17 mole) of acetaldehyde, 59.8 g. (0.53 mole) of chlorobenzene and 89 ml. of 15% fuming sulfuric acid were taken. In a final experiment acetal instead of acetaldehyde was used, but again the only product was a black resinous mass; 20 g. (0.17 mole) of acetal, 59.8 g. (0.53 mole) of chlorobenzene, and 89 ml. of 15% fuming sulfuric acid were taken.

Ethylidene Chloride plus Chlorobenzene.—To a mixture of 316.8 g. (2.8 mole) of chlorobenzene and 39.9 g. (0.3 mole) of aluminum chloride in a 500-ml. three-neck flask was added dropwise 59.4 g. (0.6 mole) of ethylidene chloride during one hour. The reaction was stirred and cooled in an ice-bath to 0–10°. After an additional one-half hour the mixture was hydrolyzed with 200 g. of ice and 75 ml. of concentrated hydrochloric acid. After washing and drying the product was distilled at 162–166° (6 mm.) to give 77 g. (51%) of a yellow, blue-fluorescent oil; $n^{20}D$ 1.5961. A resinous distillation residue of 21 g. was also strongly fluorescent. Oxidation to the ketone and analysis for chlorine indicated that 1,1-di-(*p*-chlorophenyl)-ethane was present.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: Cl, 28.24. Found: Cl, 28.27, 28.30.

The attempted purifications with sulfuric acid and picric acid were as follows: 72 g. of the crude ethane and an equal volume of 80% sulfuric acid were stirred at room temperature for ten hours. The acid layer was discarded, fresh acid added and the treatment continued for twelve hours. After washing, drying, and distilling there was obtained 53.5 g. at 162–163° (6 mm.), $n^{20}D$ 1.5942, and a distillation residue of 15 g. The fluorescence was still apparent but less intense than that of the original. A mixture of 15 g. of this material, 10 g. of picric acid and 100 ml. of alcohol was refluxed one hour, cooled, and filtered. After washing and drying the filtrate it was distilled at 156–157° (4 mm.); $n^{20}D$ 1.5947. The distilled oil showed no decrease in fluorescence and did not crystallize at 0–10°.

4,4′-Dichlorobenzohydryl Chloride plus Methylmagnesium Bromide.—To 30 g. (0.11 mole) of the chloride (m. p. 58–60°)[9] in 200 ml. of dry ether was slowly added 50 ml. of 2.40 *N* methylmagnesium bromide (0.12 mole) at 0–10°. No reaction appeared to take place but on allowing the mixture to come to room temperature the ether refluxed vigorously and a white granular precipitate formed. After hydrolysis with 200 g. of ice, 200 ml. of water, and 20 g. of ammonium chloride, a white precipitate formed. Evaporation of the ether layer gave 2 g. of an oily low-melting solid which appeared to be mostly the original chloride. The insoluble product consisted of 24.8 g. which in a melting point determination started to decompose at about 300°, turned dark red and appeared to evolve gas at 327–328°. Crystallization from nitrobenzene did not alter the melting point behavior, which corresponds to that described for *sym*-tetra-(*p*-chlorophenyl)-ethane.[9] The yield of ethane calculated on the chloride taken was 95%. A second experiment in which the order of addition of the reactants was reversed gave the same result.

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[8] Shriner and Fuson, "Identification of Organic Compounds," second edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 149.

[9] Montagne, *Rec. trav. chim.*, **25**, 394 (1906).

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Chemical Nature of the Insecticidal Principle in Mamey Seed

BY MERRIAM A. JONES AND HAROLD K. PLANK

On account of the scarcity of plant insecticides, such as pyrethrum and rotenone, considerable interest has centered in the possible value of other sources, especially those plants already established in the western hemisphere. Among such plants is the mamey tree (*Mammea americana* L.) various parts of which have been used and some found to be highly toxic to certain insects.[1] The

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[1] H. K. Plank, *J. Econ. Entomol.*, **37** (6), 737–739 (1944).

most toxic part of this plant thus far tested was the kernel of the mature seed. The Durham and red-color tests for rotenone were negative. The marked paralytic action of the ground dry seeds suggested the presence of pyrethrins or similar compounds and led to the isolation of the toxic fraction and studies of its character with the following results.

Similarity to pyrethrins was noted in the solubility of the toxic material in various organic liquids. Petroleum ether extractives could be handled like pyrethrins for the removal of fats, waxes and fatty acids in the manner described by LaForge and Haller,[2] with the final residue, corresponding to a concentrate of pyrethrins I and II, containing the toxic principle intact. Considerable insoluble matter was deposited when the resins were left in petroleum ether at room temperature. Hydrolysis of the purified resin by refluxing one and one-half hours with 0.5 *N* sodium hydroxide followed by acidification and extraction with petroleum ether, resulted in a non-toxic resin. Inasmuch as the original toxic fraction did not contain nitrogen and therefore its toxicity was not due to an alkaloid or an amide, the evidence indicated that the toxicity may be due to an ester whose component alcohol and acid were non-toxic. The powder also was found to give an analysis for pyrethrins I and II of 0.05 and 0.14%, respectively, by the AOAC method[3] which, however, is not a positive test for pyrethrins in material other than that from *Chrysanthemum cinerariaefolium* Vis.

A principal point of difference from pyrethrins was in the change of color that took place during analysis for pyrethrins; upon the addition of Denigè's reagent the mamey material remained yellow, while pyrethrins change color from white to pink, to red, to violet and finally to blue. The absence of methoxyl in the resins was shown by analysis. The preparation of the semicarbazone from the resins by the method of Staudinger and Harder as given by Gnadinger[4] yielded no crystallizable derivative. However, after purification of the resins by nitromethane extraction of the toxic principle from a petroleum ether solution, the solvent was displaced by methanol and treatment with semicarbazone hydrochloride and sodium acetate gave a non-crystalline, nitrogen-containing derivative that could not be washed out with water. Upon subjection of this fraction to methanolic alkaline hydrolysis, a precipitate formed which was soluble in water. Addition of acid to the solution caused turbidity which could be taken up in ether. This was, therefore, an acid and, titrated electrometrically, appeared to be monobasic. This further suggests that the toxic material was an ester.

Although some of the chemical behavior of the toxic fraction suggested pyrethrins, preliminary biological tests indicated that the toxicity could not be due to actual pyrethrin content. These tests, using methods previously outlined,[1] consisted of a comparison of an extract of mamey seed powder with that of pyrethrum flowers at several levels of concentration using two different test insects. Aliquots of both materials were mixed with an insecticidally inert marc to give powders after evaporation of the solvent. When the toxicities obtained were plotted against concentration, the use of probits and log concentration did not make the curves straight. Nevertheless, it could be seen that the curves diverged sharply as the concentration (and toxicity) increased when tested on larvae of *Diaphania hyalinata* (L.), but were practically parallel when adults of *Diabrotica bivittata* F. were used. Thus, with the former test insect the concentration, in terms of percentage of original resins restored, necessary to give 40% toxicity was 13.8 for mamey seed and 2.6 for pyrethrum, signifying that the latter was 5.3 times as toxic as the former; to obtain 60% toxicity required 33% restoration for mamey seed as against 4.4% restoration for pyrethrum, thus giving a toxicity ratio of pyrethrum to mamey seed of 7.5. Against *Diabrotica* the pyrethrum was about five times as toxic as mamey seed at all levels of toxicity. If the toxicity of mamey seed were due to pyrethrins, it would be half that of the pyrethrum preparation according to analysis, and the curves representing change of toxicity with concentration for both materials would be parallel regardless of the test insect.

At the present stage of our investigations, it may be said that the toxicity of mamey seed is not due to pyrethrins but may be due to a somewhat similar type of substance.

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[2] F. B. LaForge and H. L. Haller, THIS JOURNAL, **57**, 1893–1896 (1935).

[3] Association of Official Agricultural Chemists, "Official and Tentative Methods of Analysis," 5th ed., Washington, D. C., 1940, pp. 66–67.

[4] H. Staudinger and H. Harder, *Ann. Acad. Sci. Fennicae*, **A29**, (18), 1–14 (1927). In C. B. Gnadinger, "Pyrethrum Flowers," 2nd ed., Minneapolis, 1936.

Note on a New Color Reaction of β-Chlorovinyldichloroarsine

BY HOWARD S. MASON

A project recently carried out in this Laboratory required a simple, rapid, and highly sensitive test for β-chlorovinyldichloroarsine. A test of this character has not been described in the current literature, but the findings of Baranger and Mercier[1] (who showed that in dry chloroform solution ergosterol and methyldichloroarsine produced a golden yellow color) provided the basis for an indicating reaction which met the above requirements.

It was observed that granular silica gel upon

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[1] Baranger and Mercier, *Biochem. J.*, **36**, 703 (1942).