TABLE IV

Salt	Slope	a in Å.	R in Å.
	GLYCINE		
Barium iodate[1]	0.205	4.62	3.89
Calcium iodate[1]	.205	4.62	3.89
Thallous bromide	.189	4.63	3.74
Thallous chloride	.184	4.32	3.57
Thallous iodate	.280	4.22	4.35
	ALANINE		
Barium iodate	0.166	4.88	3.60
Calcium iodate	.166	4.88	3.60
Thallous bromide	.169	4.89	3.64
Thallous iodate	.227	4.48	4.04

for the average radius. Column 4 gives the value of R calculated from slope $= 0.0625R^2/a$. The values of R are fairly constant and are of the right order of magnitude with the exception of the thallous iodate results. In order to obtain values of R in the case of thallous iodate and glycine which would be in agreement with the values of R obtained in the other cases a would have to be less than the radius of the glycine molecule. This high solubility of thallous iodate in glycine and alanine solutions may not be explained by complex ion formation between either thallous ion and glycine or iodate ion and glycine since the solubility of barium and calcium iodates and thallous bromide and chloride in glycine is normal. The results might be explained by assuming a complex ion involving thallous ion, iodate ion and glycine. Structurally this does not seem likely and since it is problematical how much weight should be placed on distances of closest approach of ions and dipolar ions it was not deemed advisable to assume such a complex ion.

Summary

The solubility of thallous bromide has been determined in potassium nitrate, glycine, alanine, and glycine containing potassium nitrate solutions. The solubility of thallous iodate was determined in glycine and in alanine solutions.

The solubility of thallous bromide and of thallous iodate in glycine and alanine solutions is discussed in relation to the Kirkwood limiting law. Thallous bromide is normal while thallous iodate shows some irregularities.

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[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF AGRICULTURE, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE]

The Formation of an Azulene on Zinc-Dust Distillation of Pyrethrosin

BY MILTON S. SCHECHTER AND H. L. HALLER

The colorless crystalline compound, named "chrysanthin" by Chou,[1] which occasionally separates from extracts of pyrethrum flowers, has recently been shown[2] to be identical with the compound pyrethrosin, obtained by Thoms[3] in 1891 from the same source. Analyses and molecular weight determinations indicate that the molecular formula of pyrethrosin is $C_{17}H_{22}O_5$.[4] The compound may be catalytically hydrogenated to a dihydro compound and also to a tetrahydro compound not previously reported. Alkaline saponification cleaves the molecule into acetic acid and another water-soluble acid which is difficult to isolate in crystalline form. The origin of the acetic acid is not evident, for the original compound cannot be obtained on acetylation of the hydrolysis product. The other acid probably results from the opening of a lactone ring. The oxygen atoms unaccounted for may be of the ether type.

In an attempt to determine the type of nucleus existent in pyrethrosin, the compound was subjected to a zinc-dust distillation in an atmosphere of hydrogen. A green oily distillate was obtained, which upon steam distillation yielded an intensely blue oil. Cold 85% phosphoric acid removed the blue compound from its petroleum ether solution, and on dilution of the acid solution with ice water the blue compound was regenerated. The yield was about 1.5% of the weight of pyrethrosin used. The blue oil was distilled under reduced pressure and further purified by passing a petroleum ether solution through a column of activated alumina (Brockmann). With trinitrobenzene an addition compound was formed, which after three recrystallizations from ethanol melted at 167–168° (cor.). Analysis showed it to possess the formula $C_{19}H_{17}N_3O_6$, from

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(1) Chou and Chu, *Chinese J. Physiol.*, **8**, 167 (1934).

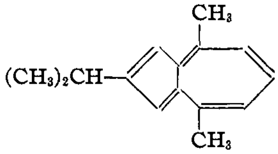
(2) Schechter and Haller, THIS JOURNAL, **61**, 1607 (1939).

(3) Thoms, *Ber. deut. pharm. Ges.*, **1**, 241 (1891).

(4) Rose and Haller, *J. Org. Chem.*, **2**, 484 (1937).

which it follows that the hydrocarbon moiety has the formula $C_{13}H_{14}$.

In general the properties of this oil were such as to indicate that it belonged to the class of intensely blue hydrocarbons known as azulenes. An absorption spectrum of the blue oil in absolute ethanol, obtained through the courtesy of R. E. Davis, of the Bureau of Animal Industry of the United States Department of Agriculture, resembled that of vetivazulene ($C_{15}H_{18}$),[5] Formula I, so much that the two curves were plotted with the same coördinates (Fig. 1). The remarkable similarity indicates that the structures of the two compounds are closely related. The curves for other azulenes show definite differences due to different arrangements of substituents. As none of the other azulenes obtained from natural products has the formula $C_{13}H_{14}$, the azulene obtained by us appears to be a new one, and the name "pyrethazulene" is suggested for it.



I

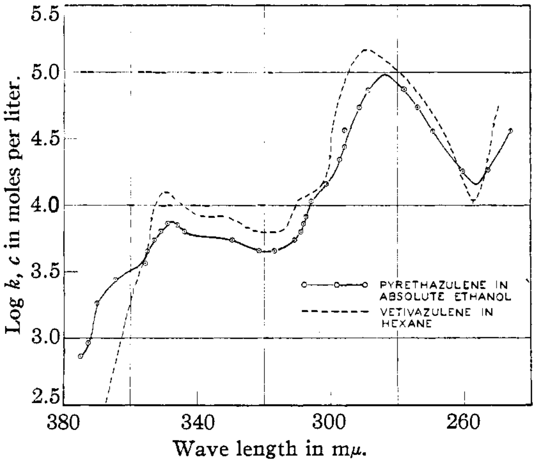


Fig. 1.—Absorption spectra of pyrethazulene and vetivazulene.

Since the parent hydrocarbon of the azulene series is $C_{10}H_8$ there are four possibilities for the type of substituents which are consistent with the formula $C_{13}H_{14}$. The compound may be a trimethylazulene, a methylethylazulene, a *n*-propylazulene, or an isopropylazulene. In an attempt to decide among these possibilities, the trinitrobenzene derivative of pyrethazulene was oxidized with aqueous potassium permanganate. The volatile acids formed were determined by the Dyer method.[6] Acetic acid was the only volatile acid formed, as proved by the slope and straightness of the distillation curve. There was no indication of the presence of any other volatile acid. The amount of acetic acid formed was 66.1% of that calculated on the basis of a trimethylazulene. If an ethyl, *n*-propyl, or isopropyl group were present, propionic acid, *n*-butyric acid, or isobutyric acid would have been formed. The formation of acetic acid only on oxidation, together with a consideration of the molecular formula, may be taken as evidence that pyrethazulene is a trimethylazulene.

From the marked similarity of the absorption spectrum of pyrethazulene to that of vetivazulene in distinction to the published curves for other azulenes, the tentative suggestion is made that the three methyl groups in the former occupy the same positions as the substituents in the latter. Thus pyrethazulene may be 2,4,8-trimethylazulene. This could be proved by a contemplated synthesis analogous to that for vetivazulene.[7]

Certain sesquiterpene compounds, such as guajol, kessyl alcohol, α-gurjunene, elemol and aromadendrene, can be dehydrogenated to azulenes by means of an appropriate dehydrogenating catalyst. Sulfur, selenium, Raney nickel and palladium-charcoal have been used for this purpose. Most azulogenic sesquiterpene compounds also give positive reactions in the color tests described by Sabetay[8] and also by Müller.[9] Pyrethrosin itself does not give either of these color reactions and apparently is not dehydrogenated to an azulene by sulfur.[10] Thus far no azulene has been produced from a compound with as many oxygen atoms as pyrethrosin.

In addition to removing oxygen from a compound, zinc dust may also act as a dehydrogenating agent.[11] This has probably taken place with pyrethrosin, although part of the dehydrogenation may have been due to the removal of oxygen from the compound as acetic acid and water. It might be possible to increase the yield of azulene

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(5) Susz, St. Pfau and Plattner, *Helv. Chim. Acta*, **20**, 469 (1937).

(6) Clark and Hillig, *J. Assoc. Official Agr. Chem.*, **21**, 684 (1938).

(7) St. Pfau and Plattner, *Helv. Chim. Acta*, **22**, 202 (1939).

(8) Sabetay and Sabetay, *Compt. rend.*, **199**, 313 (1934).

(9) Müller, *J. prakt. Chem.*, **151**, 233 (1938).

(10) Pyrethrosin also yields an azulene on dehydrogenation with palladium-charcoal, according to Nathan L. Drake of the University of Maryland, who is carrying on an investigation of the compound.

(11) Richter-Anschütz, "Chemie der Kohlenstoffverbindungen," Vol. II, part 1, p. 497 (12th ed.), 1935.

by using a more active catalyst, such as palladium-charcoal or Raney nickel.

The formation of $C_{13}H_{14}$ from $C_{17}H_{22}O_5$ shows that four carbon atoms are lost in the zinc-dust distillation. Much carbon dioxide was evolved, and according to van der Haar[12] carbon dioxide evolution indicates the presence of a carbon atom having two oxygen atoms attached to it (carboxylic acids or their esters or lactones). The loss of one carbon atom may thus be attributed to the presence of a lactone group. The formation of acetic acid accounts for two more carbon atoms. The fourth carbon atom cannot be accounted for, but it may be present in pyrethrosin as an angular methyl group.

An attempt was made to fractionate the phosphoric acid-insoluble portion of the steam-distilled oil. It distilled over a wide range, all the fractions giving a positive Sabetay[8] color reaction with a dilute chloroform solution of bromine, indicative of the presence of azulogenic compounds. Neither a trinitrobenzene nor a picric acid derivative could be prepared from any of the fractions.

Experimental

The pyrethrosin used in these experiments was purified by recrystallization from ethyl acetate with a small amount of charcoal. It melted sharply at 200–201° cor.

Tetrahydropyrethrosin.—This compound has not previously been reported. One gram of pyrethrosin dissolved in 25 cc. of glacial acetic acid was catalytically reduced, Adams platinum oxide catalyst being used. One hundred and fifty cubic centimeters of hydrogen was absorbed in two hours. Most of the acetic acid was removed under reduced pressure. The residue was taken up in ether and washed with dilute potassium carbonate solution and then with water. The ether solution was then dried over sodium sulfate and evaporated. The residue was recrystallized once from carbon tetrachloride and three times from benzene. The final recrystallization may also be made from hot water. The first few recrystallizations yielded only an amorphous product. A small quantity of the compound finally was obtained from water as white crystalline needles, m. p. 231–232°.

Anal. Calcd. for $C_{17}H_{26}O_5$: C, 65.76; H, 8.45. Found: C, 65.86; H, 8.61.

Zinc-Dust Distillation of Pyrethrosin.—Sixty grams of pyrethrosin was thoroughly mixed with 480 g. of zinc dust and distilled in three lots in an apparatus similar to that used by Phillips.[13] The Pyrex tube was 3.2 cm. in diameter and was heated by means of an electric furnace. A slow stream of hydrogen was run through the distillation tube and receiver. The temperature was observed with a 650° nitrogen-filled thermometer inserted in a Pyrex thermometer well, which projected from the inlet end of the distillation tube into the zinc dust mixture. A blue oil started to distil over at approximately 300°, and as the temperature was raised to a maximum of 550° the oil became green-brown and more viscous. There was a vigorous evolution of carbon dioxide, as shown by a heavy precipitate of barium carbonate when the outlet gas was passed through a barium hydroxide solution. An odor of acetic acid was also apparent.

Isolation of the Azulene.—The green, thick liquid which had distilled was dissolved in peroxide-free ether and washed successively with 10% potassium bicarbonate solution, 10% potassium carbonate solution, and water. Acidification of the potassium bicarbonate solution caused a slight turbidity. Acidification of the potassium carbonate solution yielded a small amount of brown oil having a phenolic odor. The oil gave a green-brown color with ethanolic ferric chloride, but the oil was too small in amount to be characterized.

From this point all operations were carried out in an atmosphere of carbon dioxide in order to protect the azulene from oxidation by air.

The ether solution was dried over anhydrous sodium sulfate, and removal of the solvent left 21.5 g. of green oil, which was steam-distilled in a stream of carbon dioxide. The distillate was received in a separatory funnel containing a layer of low-boiling petroleum ether, which separated the volatile oil from the water. The solution of steam-distilled azulene in petroleum ether was shaken with 50 cc. of ice-cold 85% phosphoric acid until all the blue color was removed from the petroleum ether. The supernatant layer was siphoned off and the phosphoric acid layer was washed three times with more solvent, which was siphoned off each time. Evaporation of the combined petroleum ether solutions yielded 8.5 g. of a mobile yellow oil.

The phosphoric acid layer was diluted first with ice and then with ice water in the presence of a layer of low-boiling petroleum ether. After thorough shaking the lower layer was discarded and the petroleum ether solution of the azulene was washed thoroughly with water. Removal of the solvent left 0.88 g. of an intensely blue oil, which was vacuum-distilled, most of it distilling at approximately 110° (p = 0.4 mm.). The amount was too small for this to be considered an accurate boiling point. A portion of this distilled oil was used to determine the absorption spectrum. The rest was dissolved in petroleum ether and chromatographed through a column of activated alumina (Brockmann) 250 mm. long and 12 mm. in diameter. The azulene, not being adsorbed very strongly, was easily washed through the column, whereas some brown and yellow impurities were strongly adsorbed in the first few centimeters of the column. The azulene was blue in dilute solutions and blue-violet in more concentrated solutions. Removal of the solvent left the intensely blue hydrocarbon.

Preparation of the Trinitrobenzene Addition Compound.—Three-tenths of a gram of the azulene purified as above was dissolved in 10 cc. of boiling ethanol and treated with a hot solution of 0.3 g. of trinitrobenzene in ethanol. On cooling, the solution set to a mass of very dark brown needles. These needles were filtered, washed with a small amount of cold ethanol, and dried. The crude product weighed 0.38 g. and melted at 158–160° with preliminary sintering at 150°. After three recrystallizations from

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[12] Van der Haar, *Rec. trav. chim.*, **48**, 1170 (1929).

[13] Phillips, THIS JOURNAL, **53**, 768 (1931).

ethanol the trinitrobenzene addition product weighed 0.17 g., sintered at 165-166°, and melted at 167-168°.

Anal.[14] Calcd. for $C_{19}H_{17}N_3O_6$: C, 59.54; H, 4.46. Found: C, 59.52, 59.57, 59.55; H, 4.49, 4.46, 4.48.

Oxidation of the Azulene.—The azulene was oxidized in the form of its trinitrobenzene derivative. Accordingly, 129.7 mg. of the purified trinitrobenzene addition product (the equivalent of 57.6 mg. of the azulene) suspended in 10 cc. of distilled water was placed in a shaking machine and oxidized by the addition of aqueous 5% potassium permanganate. Fifteen cubic centimeters of the permanganate solution was decolorized over a period of three hours; 10 cc. more was added and the mixture shaken for eighteen hours longer. Some unoxidized trinitrobenzene addition product remained, and not all the permanganate had been decolorized. Five cubic centimeters of C. P. benzene and about 130 glass beads were added and the shaking was continued for five more hours. The slight excess of permanganate was then decolorized by the careful addition of ferrous sulfate solution. The reaction mixture was separated from the beads by decantation and thorough washing. It was then made definitely alkaline with a few drops of dilute potassium hydroxide solution and boiled until all the benzene was removed. The manganese dioxide was filtered and washed, and the filtrate was subjected to analysis for volatile acids by the Dyer method.[6] Acetic acid was the only acid found. There was no indication of any other volatile acid, such as propionic, butyric, or isobutyric. The theoretical yield of acetic acid from 129.7 mg. of the trinitrobenzene addition product of a trimethylazulene is 61 mg. The amount of acetic acid actually formed in the oxidation experiment was estimated to be 40.3 mg., or 66.1% of the theoretical for a trimethylazulene.

Absorption Spectrum of Pyrethazulene.—The absorption spectrum of pyrethazulene in absolute ethanol, shown in Fig. 1, was obtained on a sample of azulene which had been purified by the phosphoric acid treatment and distilled, but it had not been chromatographed or regenerated from the trinitrobenzene addition compound by chromatography, which is the best method of obtaining the pure azulene. A quartz spectrograph with a sector photometer attachment was used. The values of the molecular extinction coefficient, *k*, were calculated from the Lambert-Beer equation

$$k = \frac{\log I_0/I}{0.434cd}$$

where *c* is concentration in moles per liter and *d* is thickness in centimeters.

An attempt was made to obtain the absorption spectrum in hexane also, but the solvent available was not suitable for spectrographic work even after treatments with sulfuric acid and with alkaline potassium permanganate. The curve obtained in this solvent ran very close to the curve obtained with ethanol to 294 mμ, at which point the solvent became practically opaque.

The Phosphoric Acid-Insoluble Fraction.—The 8.5 g. of phosphoric acid-insoluble portion of the steam-distilled oil was distilled in a 20-cm. column with a glass spiral in it. The oil distilled over a considerable range. Three fractions were taken: Fraction 1, 1.5 g., b. p. 80-120° at 25 mm., n^{26}_{D} 1.5178; fraction 2, 2.10 g., b. p. 65-85° at 0.6 mm., n^{26}_{D} 1.5498; fraction 3, 2.80 g., b. p. 85-100° at 0.6 mm., n^{26}_{D} 1.5623. In the Sabetay test[7] for azulogenic compounds fraction 1 gave a pink-violet color, fraction 2 a violet color, and fraction 3 a deep blue color. None of the fractions yielded derivatives with trinitrobenzene or picric acid.

Summary

1. Pyrethrosin, $C_{17}H_{22}O_5$, on zinc-dust distillation yields about 1.5% of a new azulene.

2. Analysis of the trinitrobenzene addition product, $C_{19}H_{17}N_3O_6$, m. p. 167-168° (cor.), indicates that the azulene has the formula $C_{13}H_{14}$.

3. Oxidation of the trinitrobenzene addition product of the blue hydrocarbon with aqueous potassium permanganate yielded acetic acid as the only volatile acid.

4. The ultraviolet absorption spectrum is remarkably similar to that for vetivazulene.

5. It is tentatively suggested that the new azulene designated "pyrethazulene" is 2,4,8-trimethylazulene.

BELTSVILLE, MARYLAND RECEIVED JULY 3, 1941

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[14] These microanalyses were made by William Stanton, of the University of Maryland.