CO_2, NH_3, H_2O, SO_2, $(C_2H_5)_2O$, CH_3Cl, CF_2Cl_2, NO, CH_3OH, C_2H_5OH). Two sets of data have been presented on diborane, saturated gas densities in their Table III[1] said to be accurate to ±3%, and unsaturated gas densities (obtained in a different apparatus) in their Table V, said to be accurate to ±1%. For convenience in comparison both these sets of data are presented in the form of compressibility factors ($z = PV/RT$ per mole) in Tables I and II. For the saturated gas densities the pressure was computed from their vapor pressure equation

$$\log P\ (\text{mm.}) = 7.185 - 782.8/(t + 273.2)$$

where t is °C. Figure 1 is a plot of z *versus* reduced pressure $P_R = P\ (\text{mm.})/30300$.

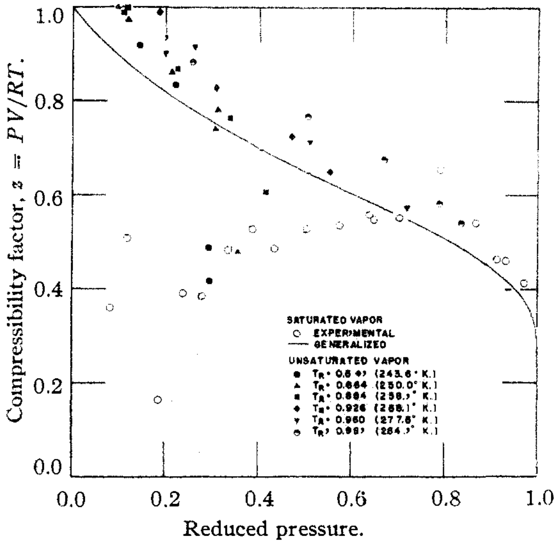

Fig. 1.—Compressibility of gaseous diborane.

It is at once evident from Fig. 1 that the data are considerably less precise than was reported; the scatter of the points for the saturated gas is quite wide, especially at the lower pressures. Another feature is the marked difference between these values for the saturated gas and those from the usual generalization below the critical point[2,3] shown as a solid line in the figure. This correlation indicates that z should decrease continuously from 1 at $P_R = 0$ to 0.70 at $P_R = 0.4$ to about 0.27 at $P_R = 1$. In contrast with this the observed results approach very low values of z at $P_R = 0$ and rise to a maximum around $P_R = 0.6$. At pressures above $P_R = 0.6$ the data and the generalized curve are in much better agreement than at the lower pressures.

The unsaturated vapor densities (except for a few values near the saturation line) are slightly lower (by 0 to 10%, average 2%) than the predicted values from the generalized correlation (Table I). The use of the Berthelot equation gives about the same results as the generalized correlation. A few examples are given in Table I.

In their pioneer studies on diborane, Stock and Kuss[5] made one measurement of vapor density: 0.0808 g. occupied 128.8 cc. at 17.3° and 405.7 mm. This corresponds to $z = 0.989$ at $T_R = 1.003$ and $P_R = 0.0134$ which is in excellent agreement with the generalized correlation (0.995) and indicates the absence of association in the vapor phase at this pressure.

It would be of interest to determine whether diborane is an exception to the generalizations as a result of some unexplained phenomenon or whether the saturated gas densities of Smith and Miller are in error.

(5) A. Stock and E. Kuss, *Ber.*, **56B**, 789 (1923).

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Experiments with Xanthotoxin and Imperatorin Obtained from the Fruits of *Ammi majus* (L.)

BY ALEXANDER SCHÖNBERG AND ALY SINA

The fruits of *Ammi majus* (L.) were described as a remedy for leukodermia in old Arabic literature.[1,2] The drug was also mentioned by Dragendorff.[3] In Egypt, the public takes the powdered fruits by mouth and then the leukodermic patches are exposed to sunlight.

Fahmy and Abu-Shady isolated[4,5] two crystalline principles from the fruits of *Ammi majus* which they named "Ammoidin" m. p. 148° and "Ammidin" m. p. 102°. We wish to thank them for allowing us to elucidate the nature of these compounds. As already stated in a previous note,[6] it was found that ammoidin and ammidin are identical with xanthotoxin[7] (Ib) and imperatorin[8] (II), respectively. In this paper, the experimental details leading to their identification are given.

Experiments with Xanthotoxin (Ib).—The demethylation of xanthotoxin was effected by heating with magnesium iodide in the absence of a solvent (compare the demethylation of khellin),[9] leading to the production of 8-hydroxy-4′,5′-6,7-furo-coumarin (Ia), also known as xanthotoxol.[10] (Ia) was converted back into xanthotoxin by the potassium carbonate–methyl iodide method; by a similar procedure the ethyl, n-pro-

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(1) Ibn El-Bitar, "Mofradat El-Adwia," Vol. I, p. 4.

(2) Dawood El-Antaki, "Tazkaret Oli El-Albab," 3rd edition, Vol. I, p. 32 (1923).

(3) "Die Heilpflanzen der verschieden Völker und Zeiten," Stuttgart, 1898, p. 488.

(4) Fahmy, Abu-Shady, Schönberg and Sina, *Nature*, **160**, 468 (1947).

(5) Fahmy and Abu-Shady, *Quarterly J. Pharmacy and Pharmacology*, **20**, 281 (1947); *ibid.*, **21**, 499 (1948).

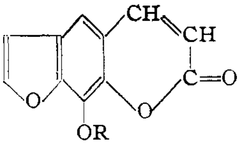
(6) Schönberg and Sina, *Nature*, **161**, 481 (1948).

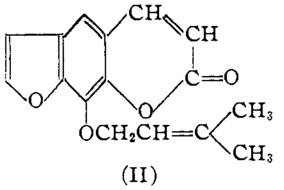
(7) Thoms, *Ber.*, **44**, 3325 (1911); Späth and Pailer, *ibid.*, **69**, 767 (1936).

(8) Späth and Holzen, *ibid.*, **68**, 1123 (1935).

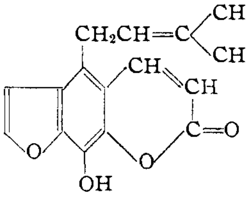
(9) Schönberg and Sina, THIS JOURNAL, **72**, 3396 (1950).

(10) Späth and Vierhapper, *Ber.*, **70**, 248 (1937).


(I)

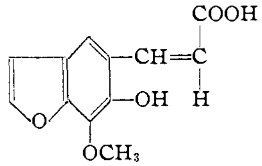

(II)

Ia, R = H
Ib, R = CH_3
Ic, R = C_2H_5
Id, R = n-C_3H_7
Ie, R = n-C_4H_9
If, R = $CH_2 \cdot COOC_2H_5$
Ig, R = $CH_2 \cdot COOH$


(III)

pyl, *n*-butyl, ω-carboethoxymethoxy ether (Ic-f) were obtained. (If) on acid hydrolysis gave the free carboxylic acid (Ig), which formed a water-soluble sodium salt.

Hydrolysis of xanthotoxin (Ib) to the corresponding coumaric acid was effected by prolonged boiling with sodium ethoxide followed by acidification. This recalls the formation of coumaric acid from coumarin by boiling with sodium ethoxide.[11] The same coumaric acid derivative was obtained by treatment of xanthotoxin with sodium sulfite solution as described by Dey and Row in the case of coumarin.[12] 6-Hydroxy-7-methoxy-5-coumaranoyl-β-acrylic acid (IV) thus obtained, is believed to be the *trans* form, since on acidification of the solution of its sodium salt it does not give back xanthotoxin.


(IV)

Experimental

Extraction of the Fruits of *Ammi majus*.—5 Kgrams of the ripe powdered fruits were extracted in a continuous hot extraction apparatus with 12 l. of petroleum ether (60–90°) for 72 hours. The deep green extract was allowed to stand for a short time and the greenish resinous crystalline "Deposit A" (rather soft due to contamination with oily impurities) was separated from the concentrated "Mother Liquor A" (about 3 l.).

"Deposit A" was washed with petroleum ether, pressed and once crystallized from alcohol giving slightly greenish crystals (34 g.), which were digested with 8 l. of boiling water and filtered hot. On cooling the aqueous solution, it gave crystals m. p. 130–140° (13.5 g.) which were recrystallized from alcohol to give colorless uniform crystals m. p. 148° (9.5 g.), not depressed by admixture with an authentic sample[13] of xanthotoxin (Ib); by working up the mother liquors a further crop was obtained (5.5 g.). On heating in vacuum the crystals sublimed unchanged; with sulfuric acid they gave an intensive yellow color. The substance did not react with diazomethane and contained no active hydrogen. *Anal.* Calcd. for $C_{12}H_8O_4$: C, 66.7; H, 3.7; mol. wt., 216. Found: C, 66.6; H, 3.8; mol. wt., 197 (Rast method).

The crystals m. p. 148°, on nitration, gave a derivative of m. p. 233° identical with nitroxanthotoxin.[7] *Anal.* Calcd. for $C_{12}H_7(NO_2)O_4$: C, 55.2; H, 2.8; N, 5.4. Found: C, 55.1; H, 2.9; N, 6.0.

"Mother Liquor A" on cooling in an ice-chest overnight, gave a crystalline "Deposit B" (12.5 g.) having a greenish color which was separated from "Mother Liquor B."

"Deposit B," was crystallized, first from alcohol and then fractionally from hot petroleum ether (60–90°) in which this substance is much more soluble than xanthotoxin. The crystals obtained from petroleum ether were recrystallized from alcohol as colorless crystals m. p. 102° (7.3 g.) not depressed by an authentic sample of imperatorin.[8] *Anal.* Calcd. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2. Found: C, 71.0; H, 5.2. With sulfuric acid, they gave an orange-yellow color.

Two grams of the substance m. p. 102° was hydrolyzed at room temperature with 20 cc. of acetic acid containing 3 drops of sulfuric acid (98%) when it gave xanthotoxol[14] (m. p. and mixed m. p.). Also when heated in a vacuum in a nitrobenzene bath for seven minutes and then sublimed in vacuum using an ethyl cinnamate bath, it gave a yellow substance m. p. 233° having all the properties of alloimperatorin (III).[14]

"Mother Liquor B": by allowing it to evaporate at room temperature, further crops of imperatorin, purified as above were obtained (2 g.) and a thick deep green oily mother liquor.

From every 100 g. of the powdered fruits, about 0.3 g. of pure xanthotoxin and 0.16 g. of pure imperatorin were obtained. Pure xanthotoxin and imperatorin are difficultly soluble in petroleum ether (60–90°), but the presence of fixed oil in the fruits increases their solubility in this solvent. Although xanthotoxin and imperatorin are more soluble in hot alcohol than in hot petroleum ether, yet alcohol suffers from the drawback that it dissolves a great amount of extractive matter, which renders the process of purification of the crystalline principles, especially that of imperatorin, very tedious. The above described procedure was based essentially on that used by Fahmy and Abu-Shady.[5]

6-Hydroxy-7-methoxy-5-coumaranoyl-β-acrylic Acids (IV).—(a) 0.2 g. of xanthotoxin was refluxed with an alcoholic solution of sodium ethoxide (2 g. sodium in 20 cc. absolute alcohol) for six hours. The solution turned yellow and after some time became turbid due to the separation of a colorless solid. The mixture was then evaporated to dryness in a vacuum and the residue dissolved in a little distilled water, concentrated again to remove most of the alcohol, then slightly acidified with hydrochloric acid under external cooling, on which a crystalline deposit was formed which was filtered off, washed with water until free from inorganic salts, dried and finally crystallized from ethyl acetate as almost colorless crystals of (IV) m. p. 218°. With sulfuric acid they turned brown and gave a yellow solution. (IV) dissolved in cold aqueous sodium bicarbonate and in dilute potassium hydroxide giving a yellow colored solution. An alcoholic solution of (IV) gave with aqueous ferric chloride a brown coloration. (IV) was easily soluble in cold alcohol, hot ethyl acetate and difficultly soluble in benzene and petroleum ether (60–90°). *Anal.* Calcd. for $C_{12}H_{10}O_5$: C, 61.5; H, 4.3. Found: C, 61.4; H, 4.2. Mol. wt. (Rast): Calcd., 234. Found, 235. Act. H.: Calcd., for 2 H, 0.86%. Found, 0.76%.

(b) Two grams of xanthotoxin was refluxed with sodium sulfite solution (2 g. in 7 cc. water) for one hour,

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(11) Fittig and Ebert, *Ann.*, **226**, 351 (1884).

(12) Dey and Row, *J. Chem. Soc.*, **125**, 554 (1924).

(13) Mixed m. p. was kindly done for us by Prof. Ebert, University of Vienna.

(14) Späth and Holzen, *Ber.*, **66**, 1137 (1933); Späth, *Monatsh.*, **69**, 75 (1936).

when it completely dissolved giving a yellow solution. The solution was concentrated until crystals appeared, acidified with hydrochloric acid, allowed to cool and left for two hours. The formed crystals were filtered off and refluxed with 6 cc. of 20% potassium hydroxide solution for one hour, cooled and acidified. The crystals obtained (from ethyl acetate) proved to be identical with *trans*-6-hydroxy-7-methoxy-5-coumaranoyl-β-acrylic acid.

Demethylation of Xanthotoxin (Ib).—A solution of 4.3 g. of (Ib) in dry benzene was added to magnesium iodide dissolved in a mixture of dry ether and benzene (from 10.16 g. iodine and 0.97 g. magnesium). The solvents were evaporated in vacuum at 120° (bath temperature) until the residue was practically dry and then further heated at 160–170° (bath temperature) for two hours. The resulting solid residue was decomposed with dilute sulfuric acid and the filtered precipitate washed with water, suspended in dilute sodium bisulfite solution, again filtered, washed with water and finally crystallized from dioxan as colorless crystals m. p. 246° which proved to be xanthotoxol (Ia)[10] (mixed m. p. and yellow color with sulfuric acid). *Anal.* Calcd. for $C_{11}H_6O_4$: C, 65.3; H, 3.0. Found: C, 65.2; H, 3.0.

Methylation of Xanthotoxol (Ia).—A mixture of 0.2 g. of (Ia), 3 g. potassium carbonate, 50 cc. acetone and 2 cc. methyl iodide was refluxed for 24 hours. The acetone filtrate and washings (20 cc. × 5) were evaporated to dryness and the residue after washing with water, separated from alcohol as colorless crystals which proved to be xanthotoxin (Ib) (m. p. and mixed m. p. and yellow color with sulfuric acid). *Anal.* Calcd. for $C_{12}H_8O_4$: C, 66.7; H, 3.7. Found: C, 66.4; H, 3.5.

Preparation of Ethers of Xanthotoxol (8-Hydroxy-4′,5′,6,7-furocoumarin) (Ia).—The preparation of the following ethers was similar to that described above in methylation of xanthotoxol. The ethers (Ic-g.), if not otherwise stated, form colorless crystals and gave with sulfuric acid a yellow color.

Ethyl Ether (Ic).—Obtained from (Ia) and ethyl iodide. It was crystallized from a mixture of benzene and petroleum ether (60–90°); m. p. 108–109°; on warming with aqueous potassium hydroxide it dissolved giving a yellow colored solution. It is difficultly soluble in petroleum ether (60–90°), easily soluble in hot benzene and hot alcohol. *Anal.* Calcd. for $C_{14}H_{10}O_4$: C, 67.8; H, 4.3. Found: C, 67.8; H, 4.2.

n-**Propyl Ether** (Id).—Obtained from (Ia) and *n*-propyl iodide. It was crystallized from petroleum ether (60–90°) after being distilled twice in vacuum, m. p. 84–85°. (Id) was easily soluble in alcohol, benzene and hot petroleum ether (60–90°). *Anal.* Calcd. for $C_{14}H_{12}O_4$: C, 68.8; H, 4.9. Found: C, 68.5; H, 5.0.

n-**Butyl Ether** (Ie).—From (Ia) and *n*-butyl iodide. It was crystallized from petroleum ether (60–90°), m. p. 83°. *Anal.* Calcd. for $C_{15}H_{14}O_4$: C, 69.8; H, 5.4. Found: C, 69.9; H, 5.4.

8-ω-Carboethoxymethoxy-4′,5′,6,7-furocoumarin (If).—Obtained from (Ia) and ethyl bromoacetate. After evaporation of acetone, the oily residue was heated in a vacuum at 140° (bath temperature) to remove excess ester. After washing with water and pressing, the solid residue separated from ethyl alcohol or petroleum ether (60–90°) as light yellow crystals of (If) m. p. 115°. *Anal.* Calcd. for $C_{15}H_{12}O_6$: C, 62.5; H, 4.2. Found: C, 62.1; H, 4.2.

8-ω-Carboxymethoxy-4′,5′,6,7-furocoumarin (Ig).—0.3 g. of (If) was dissolved in 8 cc. of glacial acetic acid and then 8 cc. of water containing 0.5 cc. sulfuric acid (98%) was added and the mixture refluxed for one hour, diluted to 50 cc. with water and allowed to stand. The crystalline deposit was filtered off, washed with water and finally crystallized from alcohol, m. p. 210°. (Ig) dissolved in sodium bicarbonate solution with evolution of gas. *Anal.* Calcd. for $C_{13}H_8O_6$: C, 60.0; H, 3.1. Found: C, 60.3; H, 3.4.

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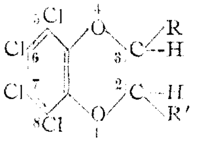
RECEIVED FEBRUARY 7, 1950

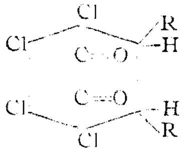
Action of Stilbene on Tetrachloro-*o*-benzoquinone

BY ALEXANDER SCHÖNBERG AND NAZIH LATIF

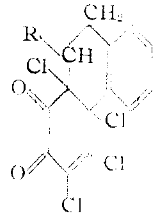
Our investigation of the photoaction of stilbene on *o*-quinones[1] has been continued with tetrachloro-*o*-benzoquinone. When stilbene and *p*-methylstilbene were used 2,3-diphenyl-5,6,7,8-tetrachlorobenzodioxene (Ia) and 2-phenyl-3-(*p*-tolyl)-5,6,7,8-tetrachlorobenzodioxene (Ib) were obtained respectively.



I



II



III

(a) R = R′ = C_6H_5
(b) R = C_6H_5; R′ = p-$CH_3C_6H_4$

Ia was obtained in a dark reaction using boiling benzene as a solvent whereas, so far, all reactions between *o*-quinones and ethylenes leading to dioxens were carried out as photoreactions. Ia on heating decomposes with the formation of stilbene. Ia and Ib are colorless substances. Ia does not form a quinoxaline derivative when treated with *o*-phenylene diamine; thus excluding formula II or III (R = phenyl or *p*-toly) of a diketone.

Experimental

Pure benzene, dried over sodium, was used. The photochemical reactions were carried out in sealed Pyrex tubes under carbon dioxide.

Photoreactions of Tetrachloro-*o*-benzoquinone. (I) **With Stilbene.**—Tetrachloro-*o*-quinone (1 g.)[2] and stilbene (0.8 g.) in benzene (30 cc.) were exposed to sunlight for thirteen days (November). Most of the benzene was then driven off; after cooling a few drops of acetone were added when colorless crystals were obtained which were recrystallized from acetone. The addition product Ia formed colorless crystals m. p. about 172°. It gave no color reaction with concd. sulfuric acid.

Anal. Calcd. for $C_{20}H_{12}Cl_4O_2$: C, 56.3; H, 2.8. Found: C, 57.0; H, 2.9.

(II) **With *p*-Methylstilbene.**—Tetrachloro-*o*-quinone (0.6 g.) (ref. 1) and *p*-methylstilbene (0.5 g.)[3] in benzene (25 cc.) were exposed to sunlight for ten days (December). The benzene was filtered, evaporated and the residue extracted with hot petroleum (60–80°). The residue was dissolved in boiling absolute alcohol and left to cool. Pale yellow crystals separated which were recrystallized from benzene–methyl alcohol. Ib formed colorless crystals m. p. 132°.

Anal. Calcd. for $C_{21}H_{14}Cl_4O_2$: C, 57.2; H, 3.1; Cl, 32.2. Found: C, 57.4; H, 3.4; Cl, 31.7.

Reaction between Tetrachloro-*o*-quinone and Stilbene in the Dark.—Tetrachloro-*o*-quinone (1.2 g.) and stilbene (0.9 g.) in benzene were refluxed for fifteen hours in the dark. The benzene was filtered, evaporated and the residue left to cool. A few cc. of acetone were then added when almost colorless crystals were obtained. Ia was re-

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(1) Compare Schönberg and Mustafa, *Chem. Rev.*, **40**, 181 (1947).

(2) Jackson and MacLaurin, *Am. Chem. J.*, **37**, 7 (1907).

(3) Meerwein, *et al.*, *J. prakt. Chem.*, **152**, 237 (1939).