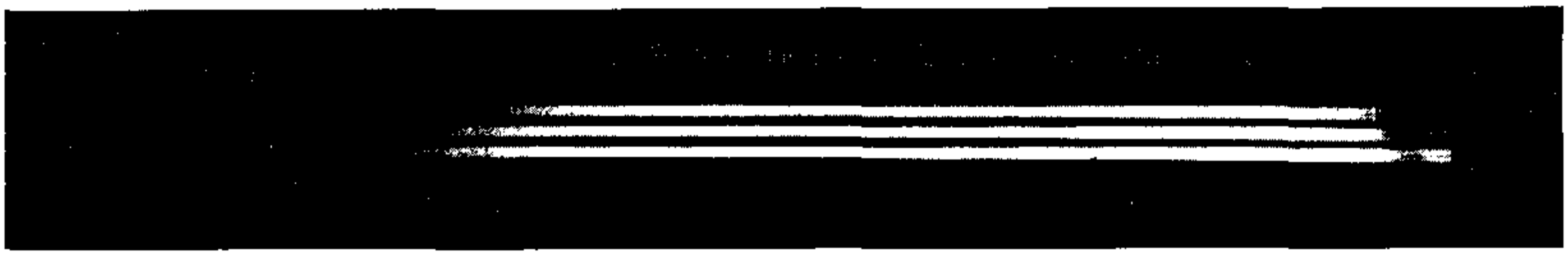

Fig. 2.

however, by cooling with water. This can be done by placing the lower end of the tube in a can with a hole in it to accommodate the window. The window is cemented into the hole with glyptal, and running water is passed through the can. This system has not been found necessary in this Laboratory. The intensity of our arc is such that even now, at the end of three years, our longest exposures for ordinary unsensitized ortho plates are of the order of three minutes, and our shortest five seconds. For these periods no cooling is needed.

Figure 2 shows a series of exposures taken with a medium quartz spectrograph (Hilger E 3) through a Spekker, for five, ten, and twenty seconds, using a non-sensitized DC ortho plate, and D 72 developer.

For use with the Spekker, this tube of course needs just as careful a system of adjustment as any spark source, because the point of light coming from the end of the capillary has to be exactly opposite the edge of the prism in the Spekker, and the axis of the capillary has also to be in exact alignment with the path of the light into the Spekker. A rigid but adjustable mounting is afforded by a device consisting of a solid base with two rigid iron uprights which hold the vertical cylinders of the tube. A shelf is built in between the two supports for the hydrogen reservoir to rest upon. The position of the base is adjusted by three thumb screws with lock nuts, which should be provided with a vernier. The spectrograph, the Spekker photometer, and the mounting for the hydrogen discharge tube are all carried on a steel I-beam, which makes an ideal optical bench.

The design and construction of this hydrogen discharge tube would have been impossible without the advice and assistance of Dr. Gordon L. Locher.

RECEIVED FEBRUARY 23, 1940

On Brassicasterol, the Characteristic Sterol of Rapeseed Oil[1]

BY ERHARD FERNHOLZ AND HOMER E. STAVELY

In the year 1906 Windaus and Hauth[2] discovered that phytosterol obtained from calabar beans contained a doubly unsaturated component characterized by the formation of a sparingly soluble acetate tetrabromide. The new sterol was named stigmasterol, after the botanical name of the calabar bean, *Physostigma venenosum.* Various workers have since investigated phytosterols from different sources by this bromination method. The formation of the characteristic insoluble tetrabromide of the acetate has often been and sometimes still is considered sufficient evidence for the presence of stigmasterol. An early paper by Windaus and Welsch[3] describes a sterol occurring in rapeseed oil which forms an acetate tetrabromide difficult to distinguish from the stigmasterol derivative. This sterol was named brassicasterol from its origin (*brassica rapa*). The following table gives a comparison of the properties of stigmasterol and brassicasterol and some derivatives.

TABLE I

M. p. of............	Stigmasterol	Brassicasterol
Sterol	**170**	**148**
Acetate	**142**	**158**
Propionate	**122**	132
Benzoate	160	167
Acetate tetrabromide	205–212	205–213

It is obvious that the mere isolation of an acetate tetrabromide of the proper melting points is not enough to establish the existence of stigmasterol in a mixture of plant sterols, since it could equally well be brassicasterol. However, debromination would enable an investigator to distinguish between stigmasteryl acetate and brassicasteryl acetate. Brassicasterol has received little attention since its first isolation in 1909. Some years ago Schmid and Waschkav[4] investigated the tetrabromide by crystallographic methods and found it indistinguishable from stigmasteryl acetate tetrabromide. We are unaware of other publications concerning brassicasterol. In the last few years degradation methods for sterols have been greatly improved, and we thought that in spite of the difficulty of preparing large amounts of brassicasterol the few grams we had on hand would be sufficient for the investigation of its structure. The close similarity of stigmasterol and brassicasterol suggested application

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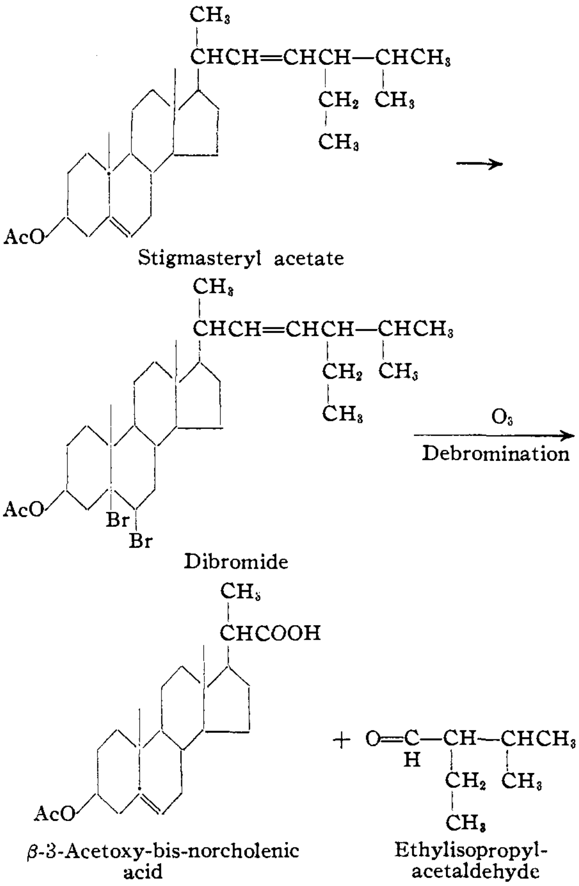
(1) Given at the Cincinnati meeting of the American Chemical Society, Food and Agricultural Division.

(2) Windaus and Hauth, *Ber.*, **39**, 4378 (1906).

(3) Windaus and Welsch, *ibid.*, **42**, 612 (1909).

(4) Schmid and Waschkav, *Monatsh.*, **48**, 139 (1927).

of the ozonization methods used by one of us in the determination of the structure of stigmasterol.



Stigmasteryl acetate

Dibromide

β-3-Acetoxy-bis-norcholenic acid

Ethylisopropyl-acetaldehyde

In the case of brassicasterol the result was quite similar, except that in place of ethylisopropyl acetaldehyde methylisopropylacetaldehyde was formed.

The latter aldehyde is known to be a splitting product of ergosterol and its semicarbazone was identical in every respect with that of the aldehyde from highly purified brassicasterol, as Table II demonstrates. Brassicasterol is closely related to ergosterol, and could be named 7,8-dihydroergosterol. On catalytic hydrogenation both sterols give the same saturated sterol, ergostanol.

TABLE II

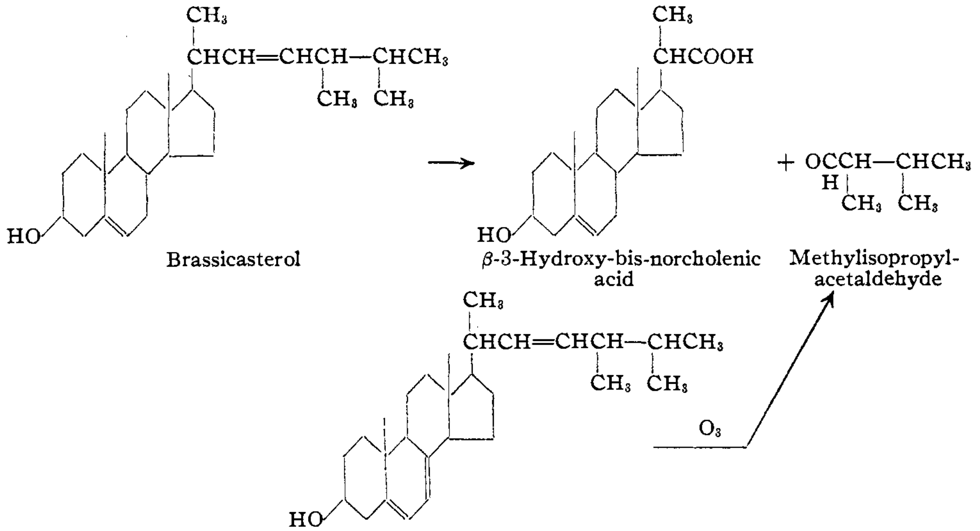
SEMICARBAZONE OF ALDEHYDE

	Ergosterol	Brassicasterol
M. p., °C.	128	128
[α]D	−52	−50

COMPARISON OF ERGOSTANOL AND BRASSICASTANOL

	M. p.	[α]D	M. p.	[α]D
Stanol	144	+15	143	+16
Acetate	145	+ 6	145	+ 7
m-Dinitrobenzoate	203	+13	202	+13

To obtain satisfactory agreement of the constants as shown in Table II, it was necessary to use brassicasterol of highest purity. This was finally obtained by numerous crystallizations of the acetate tetrabromide. Before realizing this we carried out a number of hydrogenation and ozonization experiments with the result that the hydrogenation products differed in rotation from ergostanol, but more noteworthy, the semicarbazone of the aldehyde had a lower rotation and a lower melting point. Both constants agree with those of the partially racemized aldehyde. It seems probable to us that the cruder preparations of brassicasterol contain an isomer differing in the configuration of C_{24}, and we are now engaged in the investigation of this question. The fact that



Brassicasterol

β-3-Hydroxy-bis-norcholenic acid

Methylisopropyl-acetaldehyde

Ergosterol

a derivative of ergosterol (C_{28}) exists in higher plants is not surprising since it has been shown that ergosterol, itself, is present in numerous phytosterols. Cottonseed sterols have been reported to contain 5% of ergosterol.[5] We have some indication that Δ^5-ergostenol comparable in structure to β-sitosterol and cholesterol also exists in nature, although its isolation in pure form has not yet been accomplished.

(5) Windaus and Bock, *Z. physiol. Chem.*, **250**, 258 (1937).

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Photochemical Investigations. V. The Photolysis and Iodine Sensitized Decomposition of Gaseous Ethylene Iodide

By Willard H. Janneck and Edwin O. Wiig

The thermal decomposition of ethylene iodide has been investigated in the gas phase[1] at 195–230° and in carbon tetrachloride solution[2] at 40–152°. A comparison by extrapolation of the rates in the gas phase and in solution shows that the reaction is apparently the same in both phases. The direct[3] and iodine sensitized[4] photolyses of ethylene iodide have been done in carbon tetrachloride solution but, prior to this work, not in the gas phase.

Experimental

The all-glass reaction system, which was sealed off from the main pumping line during each run, consisted of a 500 cc. flask which could be evacuated to 10^{-3}–10^{-4} mm., a magnetic hammer to break ampules containing a weighed amount of ethylene iodide, and an α-bromonaphthalene manometer connected to the flask through a long spiral of capillary tubing. This tubing and a buffer of ethylene prevented ethylene iodide and iodine from diffusing into the manometer. The reaction system, except the manometer and the exposed tubing (heated electrically), was thermostated at 80°. In order to prevent undue thermal decomposition at the start of a run, the reactants were brought rapidly to 80°. Assuming that ethylene iodide is a perfect gas and extrapolating the vapor pressure data[5] to 80°, 0.042–0.044 g. gave a pressure of about 52 mm. (all pressures on the α-bromonaphthalene scale except where noted), which was less than its saturation pressure. The initial pressures estimated from final pressure readings compared favorably with the calculated values.

The light source for the photo-sensitized decomposition was a 500-watt tungsten lamp. One run was made with the lamp and a Corning filter no. 401, which cut out all light below λ 5000 Å. A mercury arc, used with a Corning red-purple corex filter to remove visible light, was the source of ultraviolet for the direct photolysis.

Thermal Decomposition.—According to Arnold and Kistiakowsky,[1] the decomposition in the gas phase becomes heterogeneous at 195°. The time necessary to decompose thermally any amount of ethylene iodide in carbon tetrachloride solution, providing the combined and free iodine concentrations are known, can be calculated from Polissar's[2] equation. In the gas phase at 80° it was found experimentally that sixty-eight minutes were required to decompose 10% (10 to 20% decomposition), but in solution, at the same temperature and concentration, the time to decompose this same amount was calculated to be 3×10^5 minutes. Since the decomposition is probably homogeneous in solution, the gaseous thermal decomposition at 80° would appear to be heterogeneous. This heterogeneity probably accounts for the lack of agreement found in the thermal rates. At similar total pressures, the rates for the slowest and fastest runs were 0.060 and 0.144 mm./min., respectively. However, a plot of pressure increase *vs.* time gave smooth curves in all runs.

Photo-sensitized Decomposition.—Since the thermal rate of decomposition could not be reproduced, the increase in rate caused by illumination was obtained by allowing the reaction to take place in the dark (to obtain the thermal rate) before turning on the light to obtain the combined light and dark rate. In the run using light of λ = 5000 Å., the rate before illumination was 0.086 mm./min. On exposure, the rate increased to 0.129 mm./min., an increase of 0.043 mm./min. The largest thermal increase for a corresponding period in a dark reaction was 0.022 mm./min. In a similar manner but with the full light of the 500-watt lamp, the increases over the thermal rates were 0.153, 0.157, 0.144 mm./min. for three experiments.

The large increase in rate with the full light of the 500-watt lamp is caused only partially by the blue light made available by removal of the filter. The maximum transmission of the green filter was only about 20% at 5300 Å.; therefore the removal of the filter increased the intensity in this region fivefold, and most of the increase in rate is probably due to this increase in intensity.

The mechanism given for the sensitized reaction

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(1) Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

(2) Polissar, This Journal, **52**, 956 (1930).

(3) De Right and Wiig, *ibid.*, **57**, 2411 (1935).

(4) Schumacher and Wiig, *Z. physik. Chem.*, **11B**, 45 (1930).

(5) Mooney and Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929).