

lytic hydrogen was introduced to the cold adsorbent, to give a pressure of 2 mm. During the first seconds following the introduction of hydrogen a slight fall in pressure was observed owing to van der Waals adsorption.

Irradiation of the system, after the pressure becomes constant, with the light from a mercury lamp produces a regular and continuous decrease of pressure, which could be followed by means of a McLeod gage, during several hours. In favorable cases an irradiation of ten hours results in practically complete hydrogen adsorption. Further additions of hydrogen are adsorbed upon irradiation. Rates up to 1 cc. of hydrogen at 2.3 mm. pressure per minute, for 40 sq. cm. of irradiated surface and 18 g. of  $\text{ThO}_2$ , have been observed. In one case, more than 8 cc. of hydrogen at N. T. P. was taken up by 100 g. of thoria. Thermally activated adsorption on our thoria sample was observable at  $420^\circ$ .

Adsorption is only observable with the irradiation from a cold mercury lamp, which indicates that resonance radiation is involved and that it is atomic hydrogen which is taken up by the adsorbent. The formation of atomic hydrogen may occur in the gas phase by the Frank-Cario mechanism with excited mercury atoms. We can also imagine molecules adsorbed on the surface by van der Waals forces being dissociated by transference of energy from mercury atoms. We cannot yet decide between these alternatives. Comparison with the rate of reduction of tungstic oxide in the Frank-Cario experiment suggests a diffusion of atomic hydrogen to the surface.

At 20–30 mm. pressure no photoactivation is measurable. After subsequent lowering of the pressure to 2 mm., photoactivation is again observable, but at one-half to one-third the normal rate. We interpret this as due to an adsorbed molecular layer of hydrogen protecting the adsorption centers. Lowering the pressure does not uncover all such centers. Complete evacuation is necessary. When this is done the normal rate of photoactivated adsorption at 2 mm. pressure is found.

After many days of alternate irradiation and evacuation at  $700^\circ$  the rate of adsorption slowly decreases and falls to one-tenth of its initial value. If after evacuation at  $700^\circ$  air is introduced at atmospheric pressure and room temperature and then evacuated at room temperature, introduction of hydrogen at 2 mm. pressure followed by

resonance irradiation restores the initial rate of hydrogen adsorption. The presence of oxygen on the surface of the catalyst is thus essential. This is confirmed by the observation that thoria samples heated in hydrogen to  $700\text{--}800^\circ$  and then evacuated at this temperature do not show hydrogen adsorption on irradiation unless oxygen is again introduced. Analysis of the gas desorbed after either thermal or photoactivated adsorption shows the presence of oxygen only.

We have found an increase in the rate of thermally activated adsorption of hydrogen by chromium oxide and by reduced nickel when a certain amount of oxygen was introduced to the adsorbent.

Hedvall uses the term photoactivation of adsorption when the light is absorbed by the crystals and their activity is changed by the irradiation. We must consider, however, the cases in which adsorbent and gas are both excited by irradiation or the gas alone. In practice it will not be easy to decide between the several processes. We use the general term photo-activation of adsorption when we can measure an adsorption of gas by a surface owing to light irradiation.

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### On the Structure of Fucosterol

BY H. B. MACPHILLAMY

Fucosterol was first isolated from the alga, *Fucus vesiculosus*, by Heilbron, Phipers and Wright.<sup>1</sup> These workers showed that the sterol had the empirical formula  $\text{C}_{29}\text{H}_{48}\text{O}$  and that it was a bond isomer of stigmasterol. They further stated that both double bonds were situated in the nucleus, since treatment with ozone failed to give ethylisopropylacetaldehyde. Additional evidence indicated the absence of a conjugated system, while the ease with which stigmastanol was formed on hydrogenation showed the lack of any "inert" double bonds. Later it was proved that one of the ethylenic linkages occupied the 5-6 position.<sup>2</sup> In view of Sobotka's<sup>3</sup> suggestion that the second double bond might be located in the 11-12 position, which would render the sterol a suitable starting material for the synthesis of cortical

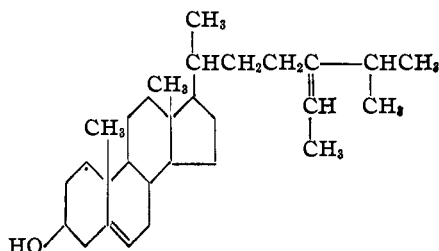
(1) I. M. Heilbron, R. F. Phipers and H. R. Wright, *Nature*, **133**, 419 (1934); *J. Chem. Soc.*, 1572 (1934).

(2) D. H. Coffey, I. M. Heilbron and F. S. Spring, *ibid.*, 738 (1936).

(3) H. Sobotka, "Chemistry of the Steroids," Williams and Wilkins Company, Baltimore, Md., 1938, p. 240.

hormones, the complete elucidation of its structure seemed desirable.

It was decided, first of all, to reinvestigate the ozonization reaction. The failure of Heilbron, *et al.*,<sup>1</sup> to isolate ethylisopropylacetaldehyde cannot be considered conclusive evidence for the lack of unsaturation in the side chain, since the later work of this author on zymosterol<sup>4</sup> has shown that side chain double bonds in sterols may occupy positions other than 22-23. The result of our study showed that fucosterol indeed presents a similar case. In two separate experiments acetaldehyde could be isolated as the *p*-nitrophenylhydrazone from the products of the ozonolysis. The yield of aldehyde was over 30% in both cases, which precludes the possibility that it may have been derived from an impurity or formed in a secondary reaction. Since position 24-28 for the double bond in question is the only one which would account for the formation of acetaldehyde by ozonolysis, it is suggested that the structure of fucosterol is best represented by the accompanying formula.



### Experimental

**Isolation of Fucosterol.**—The material used for this work was obtained from a quantity of *Fucus vesiculosus* gathered along the New Jersey coast. About 22.5 kg. of the dried sea weed was ground and percolated thoroughly with ether. After evaporation of the solvent 650 g. of extracted material remained. The residue was saponified overnight at room temperature and on purification yielded 40 g. (0.18%) of sterol. Several recrystallizations from methanol gave pure fucosterol, the physical properties of which agreed quite closely with those given by Heilbron,<sup>1</sup> as shown in the following table

	MacPhillamy M. p., °C.	[α] <sub>D</sub>	Heilbron M. p., °C.	[α] <sub>D</sub>
Sterol	124	-41	124	-38.4
Acetate	118	-45	118-119	-43.8
Benzoate	121	-16	120	..

**Ozonization of Fucosterol.**—A finely divided suspension of 1.15 g. of fucosterol in 12 cc. of glacial acetic acid was ozonized for one-half hour at an ozone concentration of about 2%, the exit gases being led through 50 cc. of water.

(4) B. Heath-Brown, I. M. Heilbron and E. R. H. Jones, *J. Chem. Soc.*, 1482 (1940).

Over-ozonization had to be avoided as it results in low if not negligible yields. The reaction mixture, combined with the wash water, was distilled through an efficient fractionating column. After approximately 20 cc. of distillate had been collected, the receiver was removed, and a solution of 500 mg. of recrystallized *p*-nitrophenylhydrazine in 20 cc. of 50% acetic acid was gradually added. The hydrazone crystallized out immediately. It was filtered, washed with cold water, and after drying weighed 175 mg. (33.6%); m. p. 124-125°. After three recrystallizations from dilute alcohol the substance had a constant m. p. of 128-129°. The melting point of a mixture with authentic acetaldehyde *p*-nitrophenylhydrazone showed no depression.

*Anal.* Calcd. for C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>: C, 53.63; H, 5.06; N, 23.45. Found: C, 53.58; H, 4.89; N, 23.69.

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### Olefin Rearrangements. The Equilibrium of Olefins from Pinacolyl Alcohol<sup>1</sup>

BY ROBERT KINSEL SMITH

The dehydration of saturated alcohols and the attendant rearrangement of olefins formed during the reaction have long been investigated experimentally. The mechanisms of these rearrangements have been studied intensively on the basis of experimental results. The absence of thermodynamical data has in general prevented the calculation of equilibrium constants for the ratios of different olefins obtained from a particular dehydration. Recently, thermal data have been published<sup>2,3</sup> concerning the heats of hydrogenation of 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene and the relative heat contents of 2,2-dimethylbutane and 2,3-dimethylbutane. These provide a basis for the calculation of the equilibrium mixture of these olefins produced in the dehydration of methyl-*t*-butylcarbinol. The equilibrium values for the ratios of the olefins obtained in this reaction are of importance because widely variant results are obtained through the use of different catalysts to effect the dehydration.

Meunier and Whitmore<sup>4</sup> dehydrated methyl-*t*-butylcarbinol with phosphoric acid on silica gel

- (1) Original manuscript received August 7, 1941.
- (2) (a) Dolliver, Gresham, Kistiakowsky and Vaughan, *THIS JOURNAL*, **59**, 831 (1937); (b) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 142 (1936).
- (3) Rossini and Prosen, *ibid.*, **62**, 2250 (1940).
- (4) Meunier and Whitmore, *ibid.*, **55**, 3721 (1933).