The Melting Point Diagram for the System *meso-dl*-Diethyl Glycol.—Known mixtures of pure *dl* and *meso* glycols sealed in small melting point tubes were heated slowly under constant agitation in a water-bath, the temperature of which was raised at the rate of 1° per five minutes. The temperatures at which the last particle of solid disappeared were recorded as the melting points and are plotted in Fig. 1. The composition of the eutectic mixture is 21.5% *meso*- and 78.5% *dl*-glycol and that of the glycol mixture (m. p. 50.4°) obtained from the hydrogenation of divinyl glycol 52% *meso* and 48% *dl*.

The divinyl glycol separated from the glycol mixture formed during the reduction of a mixture of acrolein and crotonaldehyde according to the method of Lespieau and Weimann[2] gave the same mixture of diethyl glycols as that from acrolein alone.

It may therefore be concluded that the pinacolic reduction of acrolein gives equal quantities of *meso*- and *dl*-divinyl glycol.

DEPARTMENT OF CHEMISTRY
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RECEIVED FEBRUARY 8, 1943

COMMUNICATIONS TO THE EDITOR

THE THERMODYNAMICS OF STYRENE (PHENYLETHYLENE), INCLUDING EQUILIBRIUM OF FORMATION FROM ETHYLBENZENE

Sir:

We have measured the heat capacity of styrene from 15 to 300°K., the heat of fusion, and the vapor pressure. The latter is represented between 0 and 60° by the equation

$$\log_{10} p_{\text{mm. Hg}} = -2604.67T^{-1} - 2.57692 \log_{10} T + 15.90485$$

The calculation of the entropy is summarized in Table I.

TABLE I

ENTROPY OF STYRENE

0–15°, 2 × $D(123/T)$	0.56	
15–242.47°, solid	36.82	
Fusion, 2617/242.47	10.79	
242.47–298.16°, liquid	8.61	
Liquid at 298.16°		56.78 ± 0.3 cal./deg. mole
Vaporization, 10390/298.16	34.85	
Compression, $R \ln 6.19/760$	−9.56	
Ideal gas at 1 atm.		82.07 cal./deg. mole

Since the reaction forming styrene from ethylbenzene is of considerable interest, we have calculated the equilibrium constant at various temperatures by thermodynamic methods. Measurements of the vapor pressure of ethylbenzene from 0 to 60° lead to the equation

$$\log_{10} p_{\text{mm. Hg}} = -2959.08T^{-1} - 5.8 \log_{10} T + 25.25883$$

and hence to a heat of vaporization of 10,100 cal./mole at 298.16°K. Combining this value with the observed pressure, 9.58 mm., and with the entropy of liquid ethylbenzene[1] we find for S^0_{298} 86.39 cal./deg. mole in the gas.

The heat of the reaction

$$C_6H_5CH_2CH_3 = C_6H_5CH{=}CH_2 + H_2$$

is calculable from the heats of hydrogenation of styrene and ethylbenzene.[2] Making reasonable assumptions regarding ΔC_p, we find for the temperature range 381–1000°K.

$$\log_{10} K = -5657.9T^{-1} - 6.3779 - 0.000804T + 4.3687 \log_{10} T$$

Values of the equilibrium constants calculated from this equation are tabulated in Table II.

TABLE II

DEHYDROGENATION OF ETHYLBENZENE TO FORM STYRENE

T, °K.	$-\log_{10} K$
381	10.26
400	9.48
500	6.30
600	4.15
800	1.41
1000	−0.27
(1500)	(−2.52)

Available data on the pyrolysis of ethylbenzene indicate that near-equilibrium yields were obtained at 425–550°,[3] but not at higher temperatures[4] where, however, the situation is obscured by numerous side reactions.

The details of the calorimetric work will be

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[1] Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930).

[2] Dolliver, Gresham, Kistiakowsky and Vaughan, *ibid.*, **59**, 831 (1937).

[3] Sergienko, *Compt. rend. acad. Sci.* (U. R. S. S.), **26**, 69–72 (1940); Oblad, Marschner and Hurd, THIS JOURNAL, **62**, 2066 (1940).

[4] Dobryanskiĭ, Uchenyi, Zapiski, Leningrad, Gosudarst. Univ. im. A. S. Bubnova, Ser. Khem. Nauk I, No. 1, 105 (1935); Dobryanskiĭ, *et al.*, Trans. Exptl. Research Lab. "Khimgas," Materials on Cracking and Chem. Treatment of Cracking Products (U. S. S. R.), **3**, 1 (1936); Zal'kind and Bulavskiĭ, *Plasticheskie Massui*, No. 3, 9 (1935).

presented later, together with a discussion of the molecular structure.

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LESTER GUTTMAN
EDGAR F. WESTRUM, JR.
KENNETH S. PITZER

RECEIVED OCTOBER 19, 1942

AN AMYLASE INHIBITOR FROM CERTAIN CEREALS

Sir:

In the course of an investigation of the action of salivary amylase on native wheat starch granules, it was observed that starch degradation did not occur when the wheat berry was crushed in a solution of human saliva. Degradation was rapid when starch prepared from similar grain was thus treated, but it again was inhibited by adding to it the wash liquid obtained during starch extraction.

Further studies indicated that wheat grain contains a water-soluble, protein-like substance which has a powerful inhibitory action on salivary, pancreatic, and most bacterial amylases. The substance inhibits the action of these enzymes both on gelatinized and native (raw) starch. No inhibition was observed with two commercial amylase preparations, supposedly of bacterial origin, nor with fungal nor cereal malt amylases. The sensitive amylases varied in their response; under comparable conditions equal amounts of the inhibitor gave reductions in starch dextrinization rates of 82% for salivary amylase, 48% for bacterial amylase, and 23% for pancreatic amylase.

The inhibiting substance is soluble in water and in dilute salt and dilute ethanol solutions but insoluble in petroleum ether. High levels of ammonium sulfate or of ethanol give precipitates that are active when redissolved in water. The substance is retained by a cellophane dialysis membrane. In water solution it is quite thermostable, being little affected by temperatures up to 90°. However, autoclaving for thirty minutes at 15 lb. pressure causes complete loss of inhibiting properties.

Reaction of the inhibitor with the amylase is reversible; differential alcohol solubilities have been utilized to separate a combination of the two into active inhibitor and active amylase.

The inhibitor was found in all samples of wheat and rye tested and one of similar properties in certain of the sorghums. Amylase inhibitors could not be detected in barley, oats, maize, rice, or most of the sorghums.

The inefficiency of human saliva as a hydrolytic agent for digestion of the starch of wheat or rye or of their flours may be of pronounced physiological significance. As far as starch is concerned, the recognized high nutritive value and digestibility of these cereals must be attributed to actions in regions of the digestive tract other than the mouth. The finding likewise has industrial significance, since bacterial amylases may be used as "pre-malting" agents in the current expansion of alcohol production from grain. Indications are that at least certain bacterial amylase preparations, while entirely satisfactory for pre-malting corn, would not be as applicable in the liquefaction of unautoclaved wheat mashes.

Experimental data relative to the above discussion are being prepared for publication and work in progress is designed to provide additional information relative to the nature and mode of action of the inhibiting substance.

DEPARTMENT OF AGRICULTURAL CHEMISTRY
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ERIC KNEEN
R. M. SANDSTEDT

RECEIVED MAY 10, 1943

STEROLS. CLIV. SAPOGENINS. LXVI. THE SAPOGENIN OF *TRIGONELLA FOENUM-GRAECUM*

Sir:

In the course of our plant studies during the past year we have found two hundred new sources for steroidal sapogenins. Among the plants investigated was *Foenugreek* seed, *Trigonella Foenum-Graecum*. Recently, Soliman and Mustafa [*Nature*, **151**, 196 (1943)] have reported that the sapogenin fraction from this plant contains an unknown sapogenin, m. p. 198°, of the composition $C_{27}H_{42}O_3$, having one free hydroxyl group and two inert oxygen atoms. These authors state the sapogenin "belongs to the sarsasapogenin group of sapogenins and its structure is now the subject of study."

We wish to report that we have identified the sapogenin of *Trigonella Foenum-Graecum* as diosgenin, m. p. and mixed m. p. 202° (*Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 78.3; H, 10.1). Acetylation with boiling acetic anhydride gave diosgenin acetate, m. p. and mixed m. p. 199° (*Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H. 9.7. Found: C, 76.2; H, 9.5).

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RECEIVED APRIL 12, 1943