tom of the containing vessel and consists of small glistening crystals.[4] Neither the crystalline structure nor other of the physical properties of these two modifications has been studied in any detail.

The fact that in the case of both benzalhydantoin and N-3-methylhydantoin, the white modification seems to be stable in alkaline solutions while the yellow modification is stable in an acid medium, suggests the possibility that they may represent, respectively, lactim, and lactam forms of the hydantoin molecule.

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(4) This observation was made several years ago but was not reported at the time. It was disconcerting until the fact was established that the yellow compound could be substituted for the white in reduction and alkylation reactions without apparent loss in the percentage yields.

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The Condensation of Aldol with Dimedon

BY ISAKU KASUYA

In the course of another investigation it became necessary to obtain for comparison an authentic sample of the condensation product of aldol with dimedon.

The preparation of this compound has been reported previously by Fricke[1] who obtained a product which after crystallization from 50% ethanol melted at 170–172°. He reported further that crystallization of this substance from 96% ethanol gave rise to the formation of crotonaldimedon, m. p. 183°.

The condensation product obtained by us melted at 146–148° and could be crystallized repeatedly from 96% ethanol without appreciable change.

In view of the disparity existing between these results, it seemed of interest to reinvestigate the nature of the condensation product obtained under the conditions specified by Fricke. In the light of our investigation it seems probable that the product obtained by him was an impure sample of crotonaldimedon. This result is not surprising when we consider that the reaction mixture of alcohol, aldol and dimedon is allowed to stand for several days in the presence of sodium chloride giving ample opportunity for dehydration to take place.

The author wishes to express his gratitude to Mr. Konomu Matsumura for his assistance in this investigation.

Experimental

Aldol was prepared from acetaldehyde by the method of Claisen[2] and the portion which distilled at 63–66° (6 mm.) was taken. By this method aldol was obtained as a colorless viscous liquid with a fragrant odor at room temperature, but odorless at 0°.

Condensation of Aldol with Dimedon.—A solution of aldol (0.4 g.) with dimedon (2 g.) in methanol (20 cc.) was refluxed for an hour, poured into water (500 cc.), and allowed to stand for two days. The solid which separated was crystallized from dilute (30%) methanol giving colorless prisms, m. p. 146–148°. This product was soluble in dilute sodium hydroxide.

Anal. Calcd. for $C_{20}H_{30}O_5$: C, 68.57; H, 8.57. Found: C, 68.36; H, 8.59.

Crotonaldehyde was obtained by repeated distillation of aldol. The fraction taken boiled at 100–105°.

Condensation of Crotonaldehyde with Dimedon.—A solution of dimedon (1.6 g.) in ethanol (16 cc.) was added with stirring to a suspension of crotonaldehyde (0.5 g.) in water (400 cc.). Upon standing for two days the product separated as colorless prisms, m. p. 182–186°. Upon recrystallization from ethanol it formed colorless prisms which were soluble in dilute alkali and melted at 185–186°.

Anal. Calcd. for $C_{20}H_{28}O_4\cdot 0.5C_2H_5OH$: C, 70.99; H, 8.73. Found: C, 71.14, 70.77; H, 8.98, 8.75.

Condensation of Aldol with Dimedon by the Method of Fricke.[1]—The experiment was carried out under the conditions recorded by Fricke.

The crude product melted at 160–170° with previous softening at 140°. On recrystallization from 50% ethanol it gave colorless prisms, m. p. 170–173° with preliminary softening at 160°. This product shows no depression of melting point when mixed with an authentic sample of crotonaldimedon (m. p. 185–186°). It is soluble in dilute sodium hydroxide solution.

Anal. Calcd. for $C_{20}H_{28}O_4$: C, 72.29; H, 8.43. Found: C, 72.19; H, 8.33.

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(1) Fricke, *Z. physiol. Chem.*, **116**, 129 (1921).

(2) Claisen, *Ann.*, **306**, 323 (1899).

CHEMICAL LABORATORY OF
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TOKYO, JAPAN

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The Isolation of Glutathione from Wheat Germ

BY B. SULLIVAN AND MARJORIE HOWE

In a previous contribution from this Laboratory[1] it has been shown that the harmful effect of wheat germ on the baking quality of flour is due to some compound exhibiting a very strong nitroprusside test present in the water extract of the germ. Qualitative tests indicated that this compound was glutathione and it was obtained in an impure state from the germ.

We have now succeeded in isolating glutathione from wheat germ in yields of from 0.1–0.2 g. by

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(1) Sullivan, Howe and Schmalz, *Cereal Chem.*, **13**, 665 (1936).

treating 2 kg. of fresh wheat germ with 5 liters of water and 50 g. of sulfosalicylic acid followed by filtering, centrifuging and precipitation of the supernatant liquid with neutral lead acetate. The lead precipitate was ground with 0.5 N sulfuric acid, centrifuged and filtered and the copper, mercury and silver salts precipitated successively in the usual way. The final silver salt precipitate was treated with hydrogen sulfide and filtered. Absolute ethanol was added to the filtrate and the solution evaporated rapidly to dryness in a vacuum desiccator over phosphorus pentoxide. It is very difficult to remove the last traces of ash from glutathione prepared from wheat germ and most of our preparations have contained about 1% ash. The best means of purification is through successive silver salt precipitations.

The analysis of the purified product was as follows: C, 38.86, 38.78; H, 5.49, 5.47; N(corr. 24°, 761 mm.), 13.41, 13.43. The theoretical results for $C_{10}H_{17}N_3SO_6$ are C, 39.06; H, 5.57; N, 13.68. The melting point of our preparation was 189–190° (evolution of carbon dioxide) with previous softening at 147°. Harington and Mead[2] report a melting point of 190° for pure synthetic glutathione.

The presence of glutathione in wheat germ is responsible for the deleterious action of the germ on the baking quality of flour.

[2] Harington and Mead, *Biochem. J.*, **29**, 1602 (1935).

RUSSELL MILLER MILLING CO.
MINNEAPOLIS, MINN.
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A Simplified General Equation of State

BY GEORGE WOOLSEY

A critical study of the general equation of state[1] has resulted in a slightly changed form and a simplification which makes the determination of its constants considerably less difficult. For the particular value of the critical coefficient, $n_0 = 3.25$, to which all data may be converted by means of the stretch formula, the volume coefficient, B, may be set equal to zero. The new form then becomes

$$\left(P + \frac{A}{T^{1/2}V^2 + CT^yV + DT^z}\right) V = 3.25\ T + KP + q \log\left(\frac{P}{T} + 1\right)$$

Making the equation a perfect cubic at the critical point gives the relationships

$$A = \frac{(C+2)^3}{C+3} \qquad D = \frac{1}{C+3}$$

$$K = C + 3 - n - 0.30103q = C - 0.25 - 0.30103q$$

The relationship at the Boyle temperature becomes

$$q' = \frac{A}{nT_B^{0.5}} - KT_B \text{ where } q' = 0.434294q$$

Evaluating the constants by fitting the equation at $P = 20$ and 10 at $T = 1$ makes them

$$C = 0.83429,\ D = 0.26080,\ A = 5.93811$$
$$K = 0.28694,\ q = 0.98777$$

and $T_B = 2.518$. The equation, with these constants, fits well along the entire critical isotherm.

The values of y and z can be determined by use of the relationships, $0.5 + Cy + Dz = 0$[1] and

$$\left[\left(\frac{\partial^2 P}{\partial T^2}\right)V\right]_{\mathrm{Cr}} = 0$$ [2]

From these relationships

$$0 = \frac{C+3}{C+2}\left\{\frac{C}{D}(C+D)\,y^2 + \frac{C}{D}\,y + 0.25C + 1\right\} - \frac{q'}{4}\left[\left(\frac{\partial P}{\partial T}\right)V\right]^2_{\mathrm{Cr}} - \frac{q'}{2}\left[\left(\frac{\partial P}{\partial T}\right)V\right]_{\mathrm{Cr}} + \frac{3}{4}q'$$

where

$$\left[\left(\frac{\partial P}{\partial T}\right)V\right]_{\mathrm{Cr}} = \frac{n - \frac{q'}{2}}{1 - K - \frac{q'}{2}}$$

Solving these equations, $y = 0.49736$, and $z = -3.50821$. The equation with these constants fits all regions up to $P = 86$ fairly well except for the liquid phase in equilibrium with the vapor. It can be made to fit in this last-named region by slight changes in the values of y and z, dropping only the condition that the above second derivative equal zero. Incidentally, it might be mentioned that this equation shows the existence of a unique point[3] at $P = 11$ and $T = 2$ to 3.5 as found experimentally.

Above $P = 86$ the extreme pressures seem to decrease the effective volumes of the molecules so that a new term needs to be introduced into the equation. Writing it

$$\left(P + \frac{A}{T^{1/2}V^2 + CT^yV + DT^z}\right)V = nT + \left(K - \alpha\frac{P^w}{T^x}\right)P + q\log\left(\frac{P}{T} + 1\right)$$

where α, w and x are new constants, it is possible to fit it to the high pressure nitrogen data up to $P = 433$, the limit of the experimental determinations. Work with the equation in this form indicates at present that best results are obtained

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[1] Woolsey, THIS JOURNAL, **58**, 984–987, 2229–2231 (1936).

[2] R. Plank, *Forsch. Gebiete Ingenieur.*, Band 7, 161–173 (1936).

[3] Bartlett, *et al.*, THIS JOURNAL, **52**, 1363–1381 (1930).