

tion 2. This is contrary to the conclusions of Iredale,³ who interpreted his data to mean that reaction 2 was negligible compared to the recombination. However, his data may be interpreted equally well in a second way; and in this case, the results are in accord with the findings on the photooxidation. At present, work is in progress to determine which of the two processes is predominant in methyl iodide photolysis.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIV., CALIF.

RECEIVED JULY 20, 1942

Vapor Pressures of Indene, Styrene and Dicyclopentadiene

BY P. E. BURCHFIELD

The vapor pressures of indene, styrene and dicyclopentadiene were determined over temperature ranges. The pressure-temperature data were desired for the development of distillation procedure for the separation of the components of light oil solutions.

Experimental.—The compounds used in this investigation were purified by recrystallization. The process of purification and the physical properties of the purified compounds are described elsewhere.¹ The vapor pressures were determined by the method developed by Booth, Elsey, and Burchfield.² The temperature was measured by means of a calibrated thermometer graduated to 0.1°. The necessary stem corrections were calculated and applied.

Due to the reactive nature of the compounds studied, a time factor was imposed upon the vapor pressure measurements with the exception of those of styrene. Two pressure readings, separated by a ten-minute time interval, were taken at equal temperatures for each determination. The vapor pressures of styrene at the three highest temperatures were determined by employing a new sample for each measurement, thus reducing the possibility of error through polymerization. Depoly-

TABLE I
VAPOR PRESSURE DATA OF INDENE, STYRENE AND DICYCLOPENTADIENE

Compound	Clausius-Clapeyron constants		No. 4 measurements	Temp. range of measurements, °C.	Average % deviation from mean
	A	B			
Indene	7.919	-2291	13	56.2 to 181.8	1.4
Styrene	7.929	-2103	7	33.5 to 116.3	1.1
Dichloropentadiene	7.925	-2218	6	40.1 to 90.8	0.6

(1) Smoker and Burchfield, "Cryoscopic Analysis of Light Oil Hydrocarbons," unpublished.

(2) Booth, Elsey and Burchfield, *THIS JOURNAL*, **57**, 2066 (1935).

merization was noticeable in the case of dicyclopentadiene at 100°.

The calculated constant, determined by methods of least squares, for the simplified, integrated Clausius-Clapeyron equation, and other pertinent data, are summarized in Table I.

RESEARCH DEPARTMENT
UNITED GAS IMPROVEMENT CO.
PHILADELPHIA, PA.

RECEIVED SEPTEMBER 4, 1942

A New Fructosan Isolated from *Yucca mohavensis*, Sarg.

BY KEENE P. DIMICK AND BERT E. CHRISTENSEN

Recently in connection with the chemical investigation of the *Yucca mohavensis*, Sarg. it was observed that its fructose content (3-5%) increased to as high as 60% on mild acid hydrolysis of the dried stem. This suggests the possibility of the presence of a considerable amount of fructosans which may be stored in the stem as a plant food. Further work on this material resulted in the isolation of a polyfructosan. This fructosan was first obtained from the 70% alcoholic extract of the stem of the *Yucca mohavensis* and comprised approximately 20% of the dry weight. It appeared to be similar to the compound Graminin, isolated from rye flour by Schlubach and Koenig,¹ in that it was a white hygroscopic powder, soluble in water and pyridine, and forms an addition product with ethyl alcohol.

Experimental

Isolation of the Fructosan.—The stem of the *Yucca* plant was stripped of its bark, cut into small pieces, dried at 60° and then ground in a small mill. The meal was then subjected to exhaustive and continuous extraction with petroleum ether, ether, absolute alcohol and 70% alcohol in the order given. The extract from the 70% alcohol, constituting 40% of the dry stem, was used in this study.

Twenty grams of the extract was dissolved in water and the solution made up to 100 ml. To this was added an equal volume of hot concentrated barium hydroxide suspension containing 20 g. of the hydrated base. When 200 ml. of 95% ethanol was added to this mixture, a heavy precipitate settled out. After cooling, the precipitate was removed and washed with 10% ethanol.

This material was suspended in 100 ml. of water, the barium removed with carbon dioxide, and the filtrate decolorized with 1 g. of charcoal. The compound was again precipitated with barium hydroxide and the treatment repeated.

To remove the last traces of barium the solution was treated with a small amount of dilute sulfuric acid until one drop would cause no further turbidity. By increasing the alcohol content of the aqueous solution the product was

(1) Schlubach and Koenig, *Ann.*, **514**, 182 (1934).

fractionally precipitated into three gummy fractions. It is important to precipitate the compound with alcohol in order to separate it from the small excess of sulfuric acid. If the solution is left even slightly acidic, the compound will completely hydrolyze to fructose.

The precipitate from each fraction was dissolved in a minimum of water and dried in a vacuum oven at 60°. These fractions appeared to be identical; yield 42%.

Anal. Calcd. for $(C_6H_{10}O_5)_x$: C, 44.4; H, 6.22. Found: C, 43.9; H, 6.27.

Preparation of the Acetate.—The acetylation was carried out by slightly modifying the directions of Haworth.² Three grams of the dried fructosan was added to 35 ml. of pyridine and shaken at 30° until dissolved. Thirty ml. of acetic anhydride was added slowly with stirring. The white precipitate which formed was easily redissolved. The mixture was allowed to stand at room temperature for eighteen hours and the straw colored mixture then poured into 500 ml. of ice water. The white precipitate was filtered, washed, dried over phosphorus pentoxide, and again acetylated. The acetyl content according to the method of Armstrong and Arup³ was found to be 45.4%.

Anal. Calcd. for $(C_8H_7O_6 \cdot 3CH_3CO)_x$: C, 50.0; H, 5.5; acetyl, 44.8. Found: C, 49.8; H, 5.61; acetyl, 45.4.

Preparation of the Barium Salt.—The barium salt was prepared free from barium carbonate in the following manner. Pure fructosan was dissolved in a small amount of water and an excess of saturated barium hydroxide was added. The slightly turbid solution was filtered by suction, taking precaution against the passage of air through the filter. Alcohol was added to the now clear aqueous filtrate, and the snow-white granular precipitate was filtered immediately by suction. The precipitate was washed first with 50% ethanol, and finally with 95% ethanol. The barium salt was then allowed to air dry and was finally dried completely in a vacuum oven at 50°.

Two different samples prepared in a like manner contained 22.4 and 23.5% of barium. The barium salt of the fructosan is soluble in water.

Discussion

Although sufficient data are not on hand to suggest a possible structure for this compound, a few facts have been established.

The fructosan exists in considerable quantities in the stem of the *Yucca mohavensis*. It is very readily hydrolyzed, which suggests the possibility of a fructofuranose.

The compound appears to be similar to the graminin isolated from rye flour.

Although this fructosan was first obtained from the 70% alcohol extract, in later work it was isolated from the hot aqueous extraction of the ground and dried stem.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

RECEIVED MAY 5, 1942

(2) Haworth and Percival, *J. Chem. Soc.*, 2277 (1932).

(3) Armstrong and Arup, *ibid.*, 85, 1043 (1904).

Benzylidene Aminomorpholine Compounds

By LEROY DUGAN, JR.,¹ AND HELMUT M. HAENDLER

The structure of 4-aminomorpholine suggested its possible use as a reagent for organic qualitative analysis. However, the only one of its reactions which appeared satisfactory was the condensation with aromatic aldehydes to form, in general, colorless, crystalline compounds, which may be of some value for the identification of certain specific aldehydes. 4-(*p*-Aminophenyl)-morpholine undergoes similar reactions, and also reacts with *o*-hydroxyacetophenone, but the resulting compounds will probably be useful only in isolated instances.

4-Aminomorpholine was prepared by the method of Knorr and Brownsdon² and was kept as the hydrochloride, m. p. 164–165°. Attempts to use reducing agents other than zinc and acetic acid resulted in the formation of morpholinium chloride and ammonium chloride.

The benzylidene compounds were prepared by reaction of ether or alcohol solutions of the free amine, formed from the hydrochloride by treatment with sodium hydroxide, with ether solutions of the aldehydes.

4-(*p*-Aminophenyl)-morpholine was prepared by the general methods of Kremer, Meltsner and Greenstein,³ and Lubs,⁴ m. p. 130–131°, from the nitro compound, prepared according to Harradence and Lions.⁵ The condensation products were prepared by refluxing equivalent quantities of the reactants in alcohol, followed by crystallization.

The quantitative data for the compounds formed by both of these substances are listed in Table I.

TABLE I

4-AMINOMORPHOLINE AND 4-(*p*-AMINOPHENYL)-MORPHOLINE COMPOUNDS

Carbonyl compound	Color	M. p., °C.	Nitrogen analyses, %	
			Calcd.	Found
With 4-aminomorpholine				
<i>o</i> -Hydroxybenzaldehyde	Colorless	75–76.5	13.60	13.90
<i>m</i> -Hydroxybenzaldehyde	Colorless	145–147.5	13.60	13.85
<i>p</i> -Hydroxybenzaldehyde	Tan	167–168	13.60	13.85
<i>o</i> -Nitrobenzaldehyde	Orange	99–101	17.89	17.84
<i>m</i> -Nitrobenzaldehyde	Yellow	114–114.5	17.89	17.85
Vanillin	Colorless	153–154.5	11.86	11.68
Piperonal	Colorless	76–77	11.91	12.19
With 4-(<i>p</i> -aminophenyl)-morpholine				
Salicylaldehyde	Orange	161–162	9.94	9.95
Piperonal	Tan	167.5–169	9.04	9.02
Vanillin	Yellow	205–207	8.98	9.03
Furfural	Brown	208–209	10.91	10.49
<i>o</i> -Hydroxyacetophenone	Yellow	206–207	9.43	9.52

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

RECEIVED JULY 7, 1942

(1) Present address: Chemical Warfare Service.

(2) Knorr and Brownsdon, *Ber.*, 35, 4474 (1902).

(3) Kremer, Meltsner and Greenstein, *This Journal*, 61, 2552 (1939).

(4) Lubs, U. S. Patent 2,004,763, June 11, 1935.

(5) Harradence and Lions, *J. Proc. Roy. Soc., N. S. Wales*, 70, 406 (1937).