ing to the presence of the former in small amounts. The separation is simple and not time consuming and provides a very satisfactory way to the two pure isomers. The pure 4,6-diamine is very readily obtained.

Since two good routes are available to the pure 2,4-diamine, the isolation and reduction of pure 2,4-dinitro-*m*-xylene as first described or the separation of the 2,4- from mixed diamines, selection of one over the other will depend on the particular composition of the nitrated *m*-xylene and on the quantity of 2,4-diamine desired.

Experimental

Isolation of Pure 2,4-Dinitro-*m*-xylene.—In 70 ml. of hot chloroform were dissolved 135 g. of the crude crystalline mixture of the dinitro isomers (m. p. 57–62°). This was cooled in ice. The crystals that separated as long broad plates were collected by filtration and dried (21 g.). The product sintered at 75° and melted at 81–83°. This was again crystallized from 20 ml. of chloroform. About 10 g. of solid was recovered (m. p. 82–84°). Another crystallization from 5 ml. of chloroform yielded 9.5 g. of product, m. p. 84°, and further crystallization did not effect a change in melting point. The mother liquor from the second crystallization was worked up and 9 g. more of the compound, m. p. 84°, was obtained.

This was characterized as 2,4-dinitro-*m*-xylene by reduction to the nitro amine and to the diamine. Reduction with hydrogen sulfide in warm ammoniacal solution yielded 2-nitro-4-amino-*m*-xylene which crystallized from water as golden yellow needles, m. p. 80–81°.

A suspension of 4.4 g. of the dinitro compound in 120 ml. of ethanol was hydrogenated over Raney nickel at room temperature and under a pressure of 1800 p.s.i. The theoretical amount of hydrogen was absorbed in ten to fifteen minutes. The colorless solution was filtered from the catalyst and the catalyst was washed with two 10-ml. portions of ethanol. The filtrates were combined and the ethanol was removed by distillation at reduced pressure (aspirator). The resulting viscous oil gave 3.4 g. (quantitative) of a solid on scratching with a glass rod. This was purified by crystallization from petroleum ether (b. p. 65–110°). There resulted 2.8 g. of colorless needles, m. p. 65–66°; dibenzoate, m. p. 227°; diformate, m. p. 219°.

Separation of 2,4-Diamino-*m*-xylene and 4,6-Diamino-*m*-xylene from a Mixture.—Reduction of 39.2 g. of a mixture of the dinitro isomers (m. p. 57–62°) was carried out as in the previous experiment. The temperature rose to 75° during reduction. The final product was a brownish oil weighing 28 g. After introduction of 40 ml. of concentrated hydrochloric acid, water was added until a clear solution resulted (total volume about 135 ml.). This was boiled with charcoal for fifteen minutes and filtered. Crystallization of the salt was carried out as follows: The solution was evaporated on a steam-bath until crystals began to appear. After cooling, the crystals that deposited were collected by filtration. Similar treatments with successive filtrates gave four more fractions. The fractions separated in this way weighed 11.2 g., (A); 3.4 g., (B); 11.5 g., (C); 12.0 g., (D); and 3.5 g., (E). A sample of (A) was dissolved in water, the solution made alkaline and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate, filtered and the ether evaporated. An oil resulted. By similar treatment (B) also gave an oil. Fractions (C), (D) and (E) all gave a solid, m. p. 97–110°, which, when once crystallized from petroleum ether (b. p. 65–110°), had a sharp m. p. 104°. It was the pure 4,6-diamino-*m*-xylene. Fractions (A) and (B) were combined and crystallized again as described above. The solid which separated at first weighed 4 g. By decomposition, an oil resulted which would not crystallize, but upon dissolving in petroleum ether (b. p. 65–110°) crystals were deposited. After one recrystallization, the 2,4-diamino-*m*-xylene was pure (m. p. 65–66°).

The 2,4-diamino-*m*-xylene dihydrochloride, which resulted from evaporation of a solution of (A) and (B), was recrystallized thrice from water, m. p. 317–320°.

Anal. Calcd. for $C_8H_{12}N_2 \cdot 2HCl$: C, 45.95; H, 6.75; N, 13.41. Found: C, 45.71; H, 7.05; N, 13.93.

The 4,6-diamino-*m*-xylene dihydrochloride (Fraction E) was crystallized thrice from water, m. p. 300–303°.

Anal. Calcd. for $C_8H_{12}N_2 \cdot 2HCl$: C, 45.95; H, 6.75; N, 13.41. Found: C, 45.97; H, 6.84; N, 13.39.

Satisfactory melting points for the dihydrochlorides can be obtained only by introducing the melting point tube into the bath previously heated at 295–300°. 4,6-Diamino-*m*-xylene was characterized by its dibenzoyl (m. p. 258°) and diformyl (m. p. 182–183°) derivatives.

NOYES CHEMICAL LABORATORY
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URBANA, ILLINOIS
RECEIVED OCTOBER 6, 1949

Identity of a Substance Isolated from *Cassia reticulata* Willdenow with that Isolated from *Cassia alata* L.

BY MARJORIE ANCHEL

In a recent publication[1] the isolation of unidentified "pale yellow crystals" from the leaves of *Cassia reticulata* Willdenow was mentioned in a footnote. While the structure of this compound has not yet been established, its identity with a substance obtained from the leaves of *Cassia alata* L. by Nazario and Hauptmann[2] is apparent from the following data.

			"Pale yellow crystals"	Compound of Nazario and Hauptmann
Analysis, %		Carbon	60.16	60.10
		Hydrogen	2.95	2.82
Melting point, °C.			330–340 dec. uncor.	335–336
Diazomethane product	Analysis, %	Carbon	61.93	62.23
		Hydrogen	3.94	3.63
		OCH_3	19.21	Mol. wt. 318
		Sapn. eq.	...	160.9
	Melting point, °C.		182.5–183	187

These figures agree well with the empirical formula $C_{15}H_8O_7$ (C, 60.01; H, 2.69) for the original compound, and $C_{17}H_{12}O_7$ (C, 62.18; H, 3.63; OCH_3, 18.91; mol. wt., 328) for a dimethylated product.

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(1) Anchel, *J. Biol. Chem.*, **177**, 169 (1949).

(2) Private communication from Dr. Hauptmann; see THIS JOURNAL, **72**, 1492 (1950).

THE NEW YORK BOTANICAL GARDEN
NEW YORK, N. Y.
RECEIVED OCTOBER 5, 1949

Erythrina Alkaloids. XVII. Tetrahydroerysovine

BY KARL FOLKERS AND FRANK KONIUSZY

The minimum curarizing dose of erysopine hydrochloride and of erysodine hydrochloride as determined by intralymphatic injection in frogs was found to be 4 and 10 mg./kg., respectively.[1] Hydrogenation of these two alkaloids to give tetrahydroerysopine[2] and tetrahydroerysodine[2,3] re-

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(1) Unna and Greslin, *J. Pharmacol.*, **80**, 55 (1944).

(2) Koniuszy, Wiley and Folkers, THIS JOURNAL, **71**, 875 (1949).

(3) Prelog, Wiesner, Kherana and Kenner, *Helv. Chim. Acta.*, **32**, 453 (1949).

sulted in compounds having greatly reduced curare activity. Thus, tetrahydroerysopine and tetrahydroerysodine hydrobromides showed curare activity under comparable conditions at 40 and >300 mg./kg., respectively.[1]

Erysovine differs from erysodine only in the position of one O-methyl group, and from erysopine in the number of O-methyl groups.[2] Hydrogenation of erysovine likewise resulted in the absorption of two molar equivalents of hydrogen, but the product as the free base, as well as the hydrobromide, failed to crystallize readily. Finally, tetrahydroerysovine base was obtained crystalline and pure. Under conditions where erysovine hydrochloride caused complete paralysis in all of ten frogs for one and one-half to three and one-half hours at a dose level of 2 mg./kg,, it was found that tetrahydroerysovine hydrochloride at a dose level of 1 mg./kg. caused complete paralysis of all of ten frogs for three to three and one-half hours. One-half the dose level for each alkaloid caused complete paralysis of just three of ten frogs.

Thus, conversion of erysovine into its tetrahydro derivative increases its curare activity as is the case for the hydrogenation of β-erythroidine, but contrary for erysopine and erysodine. Furthermore, tetrahydroerysovine ranks in potency with the most curare-active *Erythrina* alkaloids, namely, dihydro-β-erythroidine and β-tetrahydro-β-erythroidine.[4]

Acknowledgment.—We wish to express our appreciation to Dr. C. A. Winter and Miss E. J. Tullius of the Merck Institute for Therapeutic Research for the pharmacological test.

Experimental

Tetrahydroerysovine.—Four and one-half grams of erysovine was dissolved in 200 ml. of 1% hydrochloric acid and, after the addition of 100 mg. of Adams platinum catalyst, hydrogenation was carried out at about 40 lb. pressure. Two molar-equivalents of hydrogen was absorbed. The filtrate from the catalyst was neutralized with sodium bicarbonate and extracted with eight 10-ml. portions of chloroform. Removal of the chloroform gave a colorless gummy residue weighing 4.4 g., which was dissolved in 25 ml. of anhydrous ethyl ether. After adding 5 ml. of petroleum ether, the solvent mixture was refrigerated overnight; crystallization took place. The yield of crystals was 3.2 g.: m. p. 149–150. After two recrystallizations from ethyl ether–petroleum ether, the melting point of the tetrahydroerysovine was constant at 158–159°.

Anal. Calcd. for $C_{18}H_{25}NO_3$: C, 71.27; H, 8.30; N, 4.61. Found: C, 71.57; H, 8.17; N, 4.78.

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[4] Unna, Kniazuk and Greslin, *J. Pharmacol.*, **80**, 42 (1949).

RESEARCH LABORATORIES
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RECEIVED NOVEMBER 25, 1949

The Relationship between Molecular Weight and Polymer Viscosity for Polyisobutylene

BY F. P. BALDWIN

In 1940 Flory[1] proposed and illustrated a relationship between the weight average molecular weight, $\overline{M_w}$, of linear polyesters and their melt viscosity, η. His observations supported the relationship

$$\log \eta = A + C'\overline{M_w}^{1/2} \tag{1}$$

Eyring[2] attempted to theoretically deduce and interpret this relationship and thereafter a number of experimenters[3,4,5,6] confirmed Flory's observations for polyesters and extended his relationship to include polyethylene, dimethylsiloxane polymers and Butyl (isoprene–isobutylene copolymers).

More recently Fox and Flory[7] and Spencer and Dillon[8] have shown that this relationship breaks down for polystyrene and polyisobutylene, and the experimental data for these polymers are best represented by the relationship

$$\log \eta = A + B \log \overline{M_w} \tag{2}$$

Recent data obtained in this Laboratory for unfractionated polyisobutylenes (and two 2.5% isoprene–97.5% isobutylene copolymers) covering the molecular weight range 300,000 to 4,000,000 are in agreement with this latter relationship. The polymer viscosity data were obtained by the method of Dienes and Klemm[4] at 170°, and the intrinsic viscosities and molecular weights by the method of Flory.[9] The results are plotted in Fig. 1. Each value of intrinsic viscosity repre-

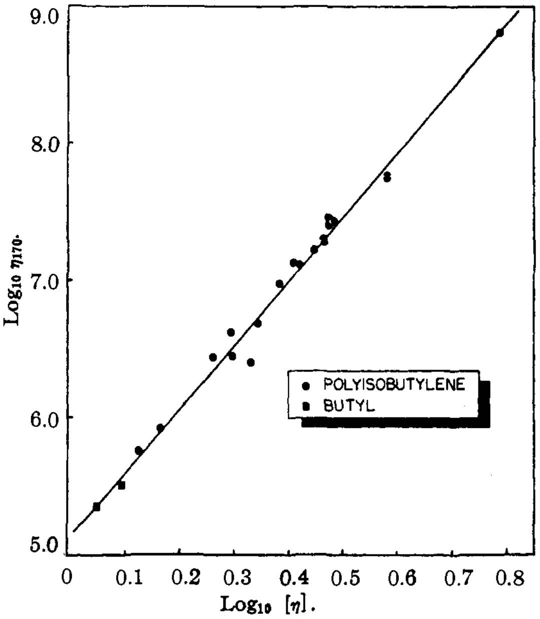

Fig. 1.

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[1] Flory, THIS JOURNAL, **62**, 1057 (1940).

[2] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 500–503.

[3] Baker, Fuller and Heiss, THIS JOURNAL, **63**, 2142 (1941).

[4] Dienes and Klemm, *J. Applied Phys.*, **17**, 458 (1946).

[5] Barry, *ibid.*, **17**, 1020 (1946).

[6] Zapp and Baldwin, *Ind. Eng. Chem.*, **38**, 948 (1946).

[7] Fox and Flory, THIS JOURNAL, **70**, 2384 (1948).

[8] Spencer and Dillon, *J. Colloid Sci.*, **4**, 241 (1949).

[9] Flory, THIS JOURNAL, **65**, 372 (1943).