PHYSICAL CONSTANTS

Molecular weight	336.85
Crystalline form and color	Amorphous white powder; slightly hygroscopic
Melting point	Caramelization begins at 270°
Solubility (g./100 ml.)	
Water, 20°	8.9
Water, 100°	21.5
95% ethyl alcohol, 20°	1.5
Ether (anhydrous), 20°	0.015
Acetone (anhydrous), 20°	0.004

As a saturated water solution cools the lactate does not crystallize. On evaporation the solution is concentrated to a semiviscous fluid containing about 100 g. lactate per 100 ml. at which time the salt begins to separate as a white amorphous floc.

In the presence of small amounts of lactic acid, gallium lactate crystallizes as thin sheets or plates when a water solution is evaporated. These crystals contain water of hydration which is lost on vacuum desiccation at 20°.

When gallium lactate is dissolved in water (25 mg./ml.) the resulting solution has a *p*H of 2.7. A solution suitable for physiological studies is prepared by dissolving the gallium lactate in boiling water, cooling and adding dilute ammonium hydroxide slowly with constant stirring to prevent any localized increase in the *p*H of the solution above 7.6. The *p*H is adjusted to 7.0–7.4 by this means. When the *p*H exceeds 8 the lactate is decomposed and if the *p*H is then lowered to 6 or 7 a gelatinous precipitate of $Ga(OH)_3$ separates.

The lactate causes no precipitation of proteins from fresh horse serum or from egg albumen solutions at *p*H 6–7. Injection subcutaneously or intravenously is tolerated by rats and rabbits with little or no localized reaction if the concentration is less than 25 mg./ml. The acutely toxic dose (LD50, 10 days) for rabbit on subcutaneous injection is 480 mg./kg. body weight. Solutions at *p*H of 7.6 and lower are not decomposed during autoclaving and sterilization although a slight increase in acidity does occur. These solutions must be stored in the cold to avoid possible mold formation.

NAVAL MEDICAL RESEARCH INSTITUTE
NATIONAL NAVAL CENTER
BETHESDA, MARYLAND

RECEIVED JULY 17, 1948

Crystalline 1,4-Anhydro-D-glucitol Tetraacetate

BY HEWITT G. FLETCHER, JR. AND CATHERINE M. SPONABLE

In a recent publication Bashford and Wiggins[1] have reported the preparation of 1,4-anhydro-D-glucitol tetraacetate as a pure sirup. Several years ago using the following procedure we obtained the same substance in crystalline form.

Eighty-four grams of powdered 1,4-anhydro-D-glucitol,[2] m. p. 113–115° (cor.), was added to a mixture of 200 ml. of acetic anhydride and 200 ml. of pyridine at 0°. After one-half hour at 5° and twenty-four hours at room temperature the reaction mixture was poured on ice and extracted with chloroform. The chloroform solution was washed with aqueous sodium bicarbonate and then with water. Removal of the solvent *in vacuo* gave a sirup which on standing in aqueous alcoholic solution at 5° eventually gave crystalline material. The product was, however, more readily purified by distillation at 2 mm. pressure and a bath temperature of 175–185°, the colorless distillate crystallizing spontaneously. Recrystallization from aqueous alcohol and from a mixture of benzene and heptane afforded large, clear rectangular prisms melting at 52–54° (cor.) and rotating in chloroform $[\alpha]^{20}D$ + 47.5° (*c*, 4.08).

Anal. Calcd. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.62; H, 6.07.

Dr. Wiggins informs us that nucleation with this material caused his sirupy 1,4-anhydro-D-glucitol tetraacetate to crystallize completely.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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RECEIVED AUGUST 3, 1948

(1) V. G. Bashford and L. F. Wiggins, *J. Chem. Soc.*, 299 (1948).

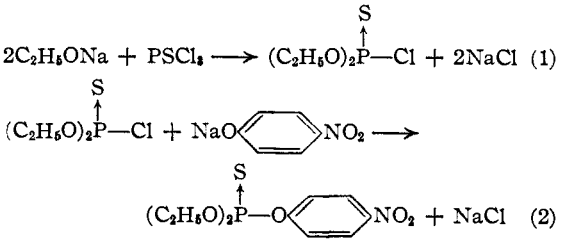
(2) We are indebted to the Atlas Powder Company for a sample of this material for which the trivial name arlitan has been proposed. *Cf.* S. Soltzberg, R. M. Goepp, Jr., and W. Freudenberg, THIS JOURNAL, **68**, 919 (1946); R. C. Hockett, M. Conley, M. Yusem and R. I. Mason, *ibid.*, 922.

Preparation of O,O-Diethyl O-*p*-Nitrophenyl Thiophosphate (Parathion)

BY JOHN H. FLETCHER, J. C. HAMILTON, I. HECHENBLEIKNER, E. I. HOEGBERG, B. J. SERTL AND J. T. CASSADAY

O,O-Diethyl O-*p*-nitrophenyl thiophosphate is reported by Martin and Shaw[1] and by Thurston[2] to possess interesting insecticidal properties, but these authors do not give detailed directions for its preparation, nor have we found this information elsewhere in the literature. We have synthesized this compound according to the general scheme proposed by German chemists[2] and have found certain modifications to be advantageous.

The reactions involved are



$$2C_2H_5ONa + PSCl_3 \longrightarrow (C_2H_5O)_2P(S)Cl + 2NaCl \quad (1)$$

$$(C_2H_5O)_2P(S)Cl + NaOC_6H_4NO_2 \longrightarrow (C_2H_5O)_2P(S)OC_6H_4NO_2 + NaCl \quad (2)$$

Sodium ethoxide (from 46 g. of sodium) in ethanol (1200 cc.) was added during three and one-half hours to a stirred solution of thiophosphoryl chloride (169.5 g.) in benzene (450 cc.), the reaction temperature being held at 5–10°. After standing several hours, the mixture was concentrated *in vacuo* to a thick slurry, and benzene (200 cc.) and water (450 cc.) were added. After shaking and separating, the aqueous layer was again extracted with benzene; the combined benzene extracts were washed with water, dried over Drierite, and concentrated *in vacuo*. Distillation of the residue using a Vigreux column gave 94 g. (50% yield) of colorless O,O-diethyl chlorothiophosphate, b. p. 71.5–72° (7 mm.), $n^{25}D$ 1.4684. Mastin and co-workers[3] give the boiling point as 96–99° (25 mm.).

Anal. Calcd. for $C_4H_{10}ClO_2PS$: Cl, 18.8; P, 16.4; S, 17.0. Found: Cl, 18.3; P, 16.2; S, 17.1.

An experiment in which the second reaction above was run at 125° in chlorobenzene, as proposed by the Germans, gave a 79% yield of parathion after fifty-one hours. We

(1) Martin and Shaw, BIOS Final Report No. 1095, Item 22, May–June 1946 (PB-78244).

(2) Thurston, FIAT Final Report No. 949, October 14, 1946 (PB-60890).

(3) Mastin, Norman and Weilmuenster, THIS JOURNAL, **67**, 1662 (1945).

found that comparable yields could be obtained in a much shorter time if ethanol or water was used as the solvent.

A mixture of O,O-diethyl chlorothiophosphate (37.7 g.), anhydrous sodium *p*-nitrophenoxide (32.2 g.), and ethanol (200 cc.) was refluxed for one hour, cooled to 20°, filtered, and the filtrate concentrated *in vacuo*. The residue was heated (oil-bath at 100–110°) with stirring at 0.5 mm. for a short period to remove any unreacted O,O-diethyl chlorothiophosphate. The crude parathion was dissolved in toluene (100 cc.) and washed with 5% sodium carbonate, then with water. After drying over Drierite and removal of the toluene at reduced pressure, the product weighed 43.5 g. (75% yield), $n^{25}D$ 1.5361. Distillation of a 200-g. sample prepared in another experiment gave 182 g. of pale yellow oil, b. p. 157–162° (0.6 mm.), $n^{25}D$ 1.5370.

Anal. Calcd. for $C_{10}H_{14}NO_5PS$: C, 41.23; H, 4.84; N, 4.81; P, 10.65; S, 11.01. Found: C, 41.38; H, 4.93; N, 4.60; P, 10.66; S, 11.06.

O,O-Diethyl chlorothiophosphate (41.6 g.) was added during one-half hour to sodium *p*-nitrophenoxide (32.2 g.) in water (100 cc.) at 95–100°, and stirring was continued at this temperature for two hours. After cooling to 20° the lower layer was separated, washed three times with water, and dried over sodium sulfate to give 37 g. (64% yield) of brown oil, $n^{25}D$ 1.5374.

STAMFORD RESEARCH LABORATORIES
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT RECEIVED OCTOBER 20, 1948

Streptomyces Antibiotics. XX. Conversion of Streptamine into Streptidine

BY FREDERICK W. HOLLY, RALPH MOZINGO AND KARL FOLKERS

Conversion of streptamine into streptidine with S-methyl isothiourea has been reported.[1] Another of the general methods for the preparation of guanidines from amines is also applicable for this conversion. Streptidine is formed when streptamine hydrochloride is heated with aqueous cyanamide. A 6% yield of streptidine, as the sulfate, was obtained by heating the mixture at 100° for forty-eight hours and a 17% yield by heating at 155° for two hours under hydrogen pressure.

Experimental

Streptidine Sulfate.—A solution prepared from 753 mg. of streptamine hydrochloride and 252 mg. of cyanamide in 2.5 ml. of water was heated for two hours at 155° under hydrogen pressure. The reaction mixture was cooled and a dark amorphous solid was removed. To the clear solution 1.0 ml. of concentrated sulfuric acid was added, and the solution was adjusted to *p*H 9 with ammonium hydroxide. The solution was concentrated under reduced pressure to a mixture of oil and crystals, and 4 ml. of 6 *N* ammonium hydroxide was added. The mixture was cooled, the crystals were collected on a filter, washed successively with water, alcohol and ether, and dried to give 180 mg. (17%) of streptidine sulfate.

Anal. Calcd. for $C_8H_{18}N_6O_4 \cdot H_2SO_4 \cdot H_2O$: C, 25.39; H, 5.86; N, 22.21. Found: C, 25.41; H, 5.60; N, 21.68.

A picrate prepared from the sulfate melted at 280–282°; when mixed with streptidine picrate, m. p. 280–282° (dec., microblock), the melting point was unchanged.

A solution containing 200 mg. of streptamine hydrochloride and 400 mg. of cyanamide in 10 ml. of water was refluxed for forty-eight hours. From the reaction mixture 14 mg. (6%) of streptidine sulfate was isolated by the procedure described above.

(1) Wolfrom and Polglase, THIS JOURNAL, **70**, 1672 (1948).

Concentration of the filtrate after removal of streptidine sulfate gave crystalline streptamine sulfate.

RESEARCH LABORATORIES
MERCK & CO., INC.
RAHWAY, NEW JERSEY RECEIVED JUNE 30, 1948

The Ultraviolet Absorption Spectrum of Gossypol[1]

BY VERNON L. FRAMPTON, JOSEPH D. EDWARDS, JR., AND HENRY R. HENZE

In the formulation of a structure for gossypol, significance was attached to the absorption maximum at approximately 250 millimicrons.[2] We find no evidence for the existence of this maximum in the absorption spectrum of gossypol.

A preparation of gossypol[3] was repeatedly recrystallized from diethyl ether–petroleum ether (30–40°) and finally from chloroform, m. p. sharp at 199°. The absorption spectrum (triangles, Fig. 1) in 95% ethyl alcohol was then determined with a Beckman quartz spectrophotometer. After additional recrystallization from diethyl ether–petroleum ether, from petroleum ether (45–90°) and finally from chloroform, m. p. sharp at 199°, the absorption spectrum (dots, Fig. 1) was again determined.

Nine different gossypol preparations,[4] each from

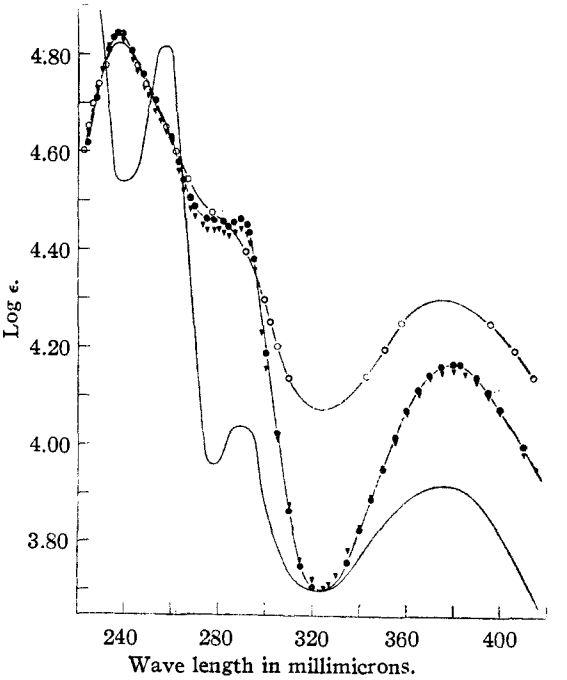


Fig. 1.—● ● ● and ▼ ▼ ▼, gossypol, authors; O O O, gossypol-acetic acid, Grunbaumowna and Marchlewski ref. 4; ——, gossypol, Adams and Kirkpatrick, ref. 1.

(1) These several data were drawn from a thesis presented by Joseph Daniel Edwards, Jr. to the Faculty of the Graduate School of the University of Texas in partial fulfillment of the requirements for the Master of Arts degree, January, 1948.

(2) Adams and Kirkpatrick, THIS JOURNAL, **60**, 2180 (1938).

(3) Campbell, Morris and Adams, *ibid.*, **59**, 1723 (1937).

(4) Dr. Boatner kindly supplied two preparations.