acetophenone and is available in a single step by Fries rearrangement of vanillin monoacetate.

A polymeric material having its proposed structure has been synthesized and properties found not to differ qualitatively or, quantitatively from those recorded for spruce lignin. Solubility characteristics and general behavior are identical and it may be methylated, acetylated and halogenated (brominated) in the same fashion giving entirely analogous derivatives. The methoxyl content is noticeably lower than the calculated values but aluminum chloride is a good demethylating agent, and the introduction of free phenol groups could easily be responsible for the darker color.

PEORIA, ILLINOIS RECEIVED AUGUST 13, 1947

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Methyl 2,4:5,6-Dimethylene-D-gluconate

BY C. L. MEHLTRETTER, R. L. MELLIES AND C. E. RIST

In an attempt to prepare polyesters of 2,4:3,5-dimethylene-D-gluconic acid by heating the methyl ester (I)[2] *in vacuo*, there was obtained by sublimation a mixture of compounds from which a new methyl dimethylene gluconate was isolated in 22% yield. This compound has now been shown to be methyl 2,4:5,6-dimethylene-D-gluconate (II). It is apparent from structures (I) and (II) that a methylene cyclic acetal rearrangement has occurred from carbons 3,5 to 5,6 of the gluconic acid chain. Cyclic acetal rearrangements were observed by Hibbert and his associates[3] who found that isomeric methylene, benzylidene and *p*-nitrobenzylidene cyclic acetals of glycerol were readily interconverted in the presence of hydrogen chloride. More recently Hann, Maclay and Hudson[4] have reported a cyclic acetal shift in the benzoylation of α-diacetone dulcitol.

The separation of the methyl dimethylene gluconate (II) from unchanged methyl 2,4:3,5-dimethylene-D-gluconate (I) and other products was effected by fractional crystallization of the sublimate mixture from methanol. The purified product, which melted at the same temperature as methyl 2,4:3,5-dimethylene-D-gluconate (152°), formed a crystalline amide and a crystalline tosyl derivative. The new product gave a specific rotation of −14.4° in methanol, as compared to +13.3° for methyl 2,4:3,5-dimethylene-D-gluconate. Efforts to establish the presence of a primary or secondary alcohol group in the methyl dimethylene gluconate by subjecting the tosylated compound to iodination by the Oldham and Rutherford[5] procedure gave only anomalous results.

The removal of a methylene group from the methyl dimethylene gluconate (II) would provide a monomethylene acetal, the structure of which if known would aid considerably in establishing the structure of the original ester. Hudson and Hann and their associates[6] have shown that the controlled acetolysis of a number of methylene sugar alcohol acetals by an acetic anhydride–acetic acid solution containing 1 to 2% sulfuric acid results in the preferential cleavage of certain methylene acetal linkages. Those formed through primary hydroxyl groups are readily cleaved. Where two secondary alcoholic acetal linkages are involved, such as in 2,4:3,5-dimethylene-D-sorbitol, the 2,4-methylene acetal ring is the more stable to acetolysis.

The acetolysis reaction was first applied to methyl 2,4:3,5-dimethylene-D-gluconate (I) to ascertain whether it would proceed according to rule. A crystalline substance was produced which was presumed to be methyl 3-acetoxymethyl-5,6-diacetyl-2,4-methylene-D-gluconate (IV). Catalytic removal of the acetyl and acetoxymethyl groups of this compound with sodium methoxide and reaction of the crude product with methanol–ammonia gave crystalline 2,4-methylene-D-gluconamide (V). The structure of the latter compound was established by the oxidative degradation of the product obtained by saponification of (IV) to 2,4-methylene-xylotrihydroxyglutaric acid. This substance was esterified and isolated as the methyl ester[7] (VII). Thus the acetolysis of methyl 2,4:3,5-dimethylene-D-gluconate results in the cleavage of only the 3,5-methylene cyclic acetal linkage as was found to be the case with 2,4:3,5-dimethylene-D-sorbitol.[6]

When analogous reactions were carried out with the methyl dimethylene gluconate, 2,4-methylene-D-gluconamide was again produced. This fact not only is evidence that the methyl dimethylene gluconate contains a 2,4-methylene acetal linkage but it also limits its structure to methyl 2,4:3,6-dimethylene-D-gluconate or methyl 2,4:5,6-dimethylene-D-gluconate (II). Conclusive proof for the latter structure was obtained from a study of

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

(2) Mehltretter, Mellies, Rist and Hilbert, THIS JOURNAL, **69**, 2130 (1947).

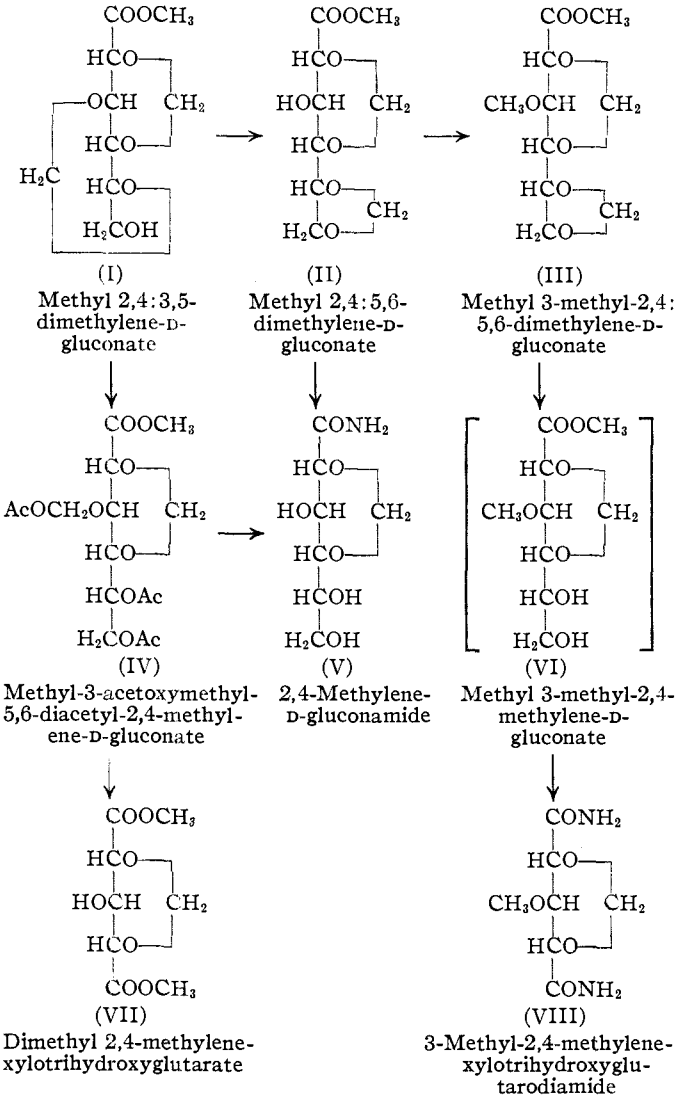
(3) Hill, Whelan and Hibbert, *ibid.*, **50**, 2235 (1928); Hibbert and Carter, *ibid.*, **50**, 3120, 3376 (1928).

(4) Hann, Maclay and Hudson, *ibid.*, **61**, 2432 (1939).

(5) Oldham and Rutherford, *ibid.*, **54**, 336 (1932); Ness, Hann and Hudson, *ibid.*, **66**, 1901 (1944).

(6) Ness, Hann and Hudson, *ibid.*, **65**, 2215 (1943); **66**, 665 and 670 (1944); Hann, Wolfe and Hudson, *ibid.*, **66**, 1898 (1944).

(7) Jones and Wiggins, *J. Chem. Soc.*, 382, 364 (1944).



the methyl ether of the methyl dimethylene gluconate (III). Acetolysis of this crystalline derivative, followed by saponification, gave a sirupy product which was oxidized with alkaline permanganate solution at 5 to 10°. The resulting acid was esterified with methanol and after treatment with methanol–ammonia yielded the diamide of 3-methyl-2,4-methylenexylotrihydroxyglutaric acid (VIII).[7] This substance could have been derived only from methyl 2,4:5,6-dimethylene-D-gluconate (II) by the series of reactions used.

Experimental

Isolation of Methyl 2,4:5,6-Dimethylene-D-gluconate (II).—Twenty grams (0.085 mole) of methyl 2,4:3,5-dimethylene-D-gluconate (I)[2] was heated for seven hours in a sublimation apparatus at 1 mm. pressure and a bath temperature of 150°. The sublimate, which consisted of both crystalline and oily substances, weighed 11.8 g. Recrystallization from methanol gave 4.4 g. (22%) of methyl 2,4:5,6-dimethylene-D-gluconate as colorless needles; m. p. 151–152°; $[\alpha]^{25}D$ −14.4° (*C*, 4.3; methanol). The melting point of a mixture of this compound with methyl 2,4:3,5-dimethylene-D-gluconate (m. p. 152–153°) was approximately 125°.

Anal. Calcd. for $C_9H_{14}O_7$: C, 46.2; H, 6.0; OCH_3, 13.3. Found: C, 46.2; H, 6.2; OCH_3, 13.4.

2,4:5,6-Dimethylene-D-gluconamide.—A 0.45-g. (0.002 mole) sample of methyl 2,4:5,6-dimethylene-D-gluconate was dissolved in 50 ml. of methanol which had been saturated with ammonia at 0°. After the solution had remained at 5 to 10° for five days it was concentrated *in vacuo* to dryness. The crude product was recrystallized from ethanol, giving 0.35 g. (83%) of 2,4:5,6-dimethylene-D-gluconamide as fine needles; m. p. 168–169°; $[\alpha]^{25}D$ +52.3° (*C*, 1.3; water).

Anal. Calcd. for $C_8H_{13}O_6N$: C, 43.8; H, 6.0; N, 6.4. Found: C, 44.1; H, 5.8; N, 6.4.

Methyl 3-Tosyl-2,4:5,6-dimethylene-D-gluconate.—To a solution of 5.85 g. (0.025 mole) of methyl 2,4:5,6-dimethylene-D-gluconate in 80 ml. of dry pyridine was added 5.50 g. (0.029 g. mole) of *p*-toluenesulfonyl chloride. After the mixture had remained at room temperature for four days it was poured into 500 ml. of ice water. The crystalline substance that precipitated (6.5 g., 67%) melted at 90–91°. After recrystallization from methanol, colorless prisms of methyl 3-tosyl-2,4:5,6-dimethylene-D-gluconate were obtained; m. p. 91–92°; $[\alpha]^{25}D$ −35.7° (*C*, 2.2; acetone).

Anal. Calcd. for $C_{16}H_{20}O_9S$: C, 49.5; H, 5.2; S, 8.3; OCH_3, 8.0. Found: C, 49.5; H, 5.1; S, 8.0; OCH_3, 7.9.

Samples of the tosylated compound upon treatment with an acetone solution of sodium iodide at 100° for two and for four hours gave, respectively, 50% and 57% of sodium *p*-toluenesulfonate. However, when the tosyl derivative was refluxed for two hours with an acetic anhydride solution of sodium iodide, 98% of sodium *p*-toluenesulfonate was obtained. A considerable quantity of free iodine was liberated in these reactions, and no desoxyiodo-derivative could be isolated.

Acetolysis of Methyl 2,4:3,5-Dimethylene-D-gluconate (I).—To 4.7 g. (0.02 mole) of methyl 2,4:3,5-dimethylene-D-gluconate was added an ice-cold acetolyzing solution consisting of 35 ml. of acetic anhydride, 15 ml. of acetic acid and 1 ml. of concentrated sulfuric acid. The resulting mixture was allowed to stand at 0° for forty-five minutes and then was agitated at room temperature for fifteen minutes to dissolve the ester completely. The solution was poured upon 400 g. of crushed ice and nearly neutralized to litmus by the addition of 70 g. of sodium bicarbonate. The white crystalline product was removed by filtration and washed with ice water. After recrystallization of the crude product from ethanol, 1.0 g. of methyl acetoxymethyl diacetyl methylene D-gluconate (probably methyl 3-acetoxymethyl-5,6-diacetyl-2,4-methylene-D-gluconate) (IV) was obtained as elongated hexagonal plates; m. p. 95–96°.

A further yield of 2.6 g. of product was obtained from the mother liquor; m. p. 95–96°. The total yield of methyl acetoxymethyl diacetyl methylene D-gluconate was 3.6 g. (48%).

Anal. Calcd. for $C_{15}H_{22}O_{11}$: C, 47.6; H, 5.9; OCH_3, 8.2. Found: C, 47.6; H, 5.7; OCH_3, 8.3.

Oxidation of the Saponified Acetolysis Product of Methyl 2,4:3,5-Dimethylene-D-gluconate.—To 12.6 g. (0.033 mole) of methyl acetoxymethyl diacetyl methylene D-gluconate obtained by acetolysis of methyl 2,4:3,5-dimethylene-D-gluconate was added 500 ml. of a solution

which contained 21.1 g. (0.067 mole) of barium hydroxide octahydrate. The latter solution was added in portions at 60° over a one-hour period so that saponification occurred gradually under conditions of low alkalinity. The barium salt was decomposed with the calculated amount of dilute sulfuric acid and the barium sulfate removed by filtration. Concentration of the filtrate *in vacuo* gave 7.0 g. of crude 2,4-methylene-D-gluconic acid as a colorless sirup. A solution of this sirup in 200 ml. of water containing 5 g. of potassium hydroxide was cooled to 5° to 10° in an ice-bath. To the stirred mixture was added a solution of 14 g. of potassium permanganate in 250 ml. of water over a period of thirty minutes. Two grams more of permanganate was introduced and the mixture stirred at 10° for one hour. Excess permanganate was destroyed with ethanol, and the manganese dioxide that had precipitated was separated by centrifugation. The clear supernatant liquor was made slightly acid to litmus with sulfuric acid and concentrated *in vacuo* to dryness. The residue was suspended in 300 ml. of methanol and 3 ml. of concentrated sulfuric acid was added with stirring. The potassium sulfate that precipitated was removed, and the solution was refluxed for seven hours. After neutralizing the sulfuric acid with barium carbonate and removing the barium sulfate by filtration the clear filtrate was concentrated *in vacuo* until crystallization occurred. The crude crystals weighed 3.8 g. and melted at 175°. Recrystallization from water gave 2.0 g. of dimethyl 2,4-methylene-xylotrihydroxyglutarate (VII); m. p. 204°; $[\alpha]^{25}D$ 0°.

Anal. Calcd. for $C_8H_{12}O_7$: C, 43.7; H, 5.5; OCH_3, 28.2. Found: C, 43.7; H, 5.3; OCH_3, 28.1.

A further quantity of product (1.5 g., m. p. 203–204°) was obtained from the original mother liquor. The diamide of 2,4-methylene-xylotrihydroxyglutaric acid was prepared from the methyl ester and melted at 286° with decomposition. The melting points of these substances agree with the values recorded by Jones and Wiggins.[7]

Acetolysis of Methyl 2,4:5,6-Dimethylene-D-gluconate (II).—A solution of 4.7 g. (0.02 mole) of methyl 2,4:5,6-dimethylene-D-gluconate in 50 ml. of an ice-cold acetolyzing mixture (35 ml. of acetic anhydride, 15 ml. of acetic acid and 1 ml. of concentrated sulfuric acid) was allowed to stand at 0° for thirty minutes and then poured into 400 ml. of ice water. The solution was neutralized to slight acidity with 70 g. of sodium bicarbonate and extracted with chloroform. The dried chloroform solution was concentrated *in vacuo* to a nearly colorless sirup (5.0 g.) which would not crystallize. The product was presumed to be methyl 5-acetoxymethyl-3,6-diacetyl-2,4-methylene-D-gluconate. In a subsequent experiment this acetolysis product was converted to crystalline 2,4-methylene-D-gluconamide by the action of methanol–ammonia.

2,4-Methylene-D-gluconamide (V). (a) From the Acetolysis Product of Methyl 2,4:3,5-Dimethylene-D-gluconate.—To 1.90 g. (0.005 mole) of methyl acetoxymethyl diacetyl methylene D-gluconate obtained by acetolyzing methyl 2,4:3,5-dimethylene-D-gluconate was added 30 ml. of chloroform. After the addition of 3 ml. of 0.2 *N* sodium methylate solution the mixture was allowed to stand at 0° for nineteen hours and was then concentrated *in vacuo* to dryness. The residue was extracted with hot ethanol and the extract concentrated to a colorless sirup (1.05 g.). A solution of 0.70 g. of this sirup in 30 ml. of methanol–ammonia was allowed to stand at 5 to 10° for two days. Concentration of the solution to dryness *in vacuo* and recrystallization of the residue from 90% ethanol gave 0.40 g. (60%) of 2,4-methylene-D-gluconamide as colorless fine needles; m. p. 195–196°; $[\alpha]^{25}D$ +55.8° (*C*, 2.1; water).

Anal. Calcd. for $C_7H_{13}O_6N$: C, 40.6; H, 6.3; N, 6.8. Found: C, 40.7; H, 6.2; N, 6.8.

It was found that methyl acetoxymethyl diacetyl methylene D-gluconate, on direct treatment with methanol–ammonia, was deacetylated and converted to 2,4-methylene-D-gluconamide.

(b) From the Acetolysis Product of Methyl 2,4:5,6-Dimethylene-D-gluconate.—To 1.0 g. of the sirup obtained from the acetolysis of methyl 2,4:5,6-dimethylene-D-gluconate was added 40 ml. of methanol which had been saturated with ammonia at 0°. After the mixture was allowed to remain at 5 to 10° for forty hours, it was concentrated *in vacuo* to dryness. The residue was recrystallized from ethanol and gave 0.3 g. of 2,4-methylene-D-gluconamide; m. p. 195–196°; $[\alpha]^{25}D$ +55.7° (*C*, 2.1; water). The melting point of this compound was not depressed when it was mixed with a sample of 2,4-methylene-D-gluconamide prepared from the acetolysis product of methyl 2,4:3,5-dimethylene-D-gluconate.

Methyl 3-Methyl-2,4:5,6-dimethylene-D-gluconate (III).—A solution of 7.8 g. (0.033 mole) of methyl 2,4:5,6-dimethylene-D-gluconate in 25 ml. of hot methanol was added to 80 ml. of methyl iodide. The resulting mixture was stirred vigorously and refluxed for six hours with 12 g. of silver oxide, the latter being added in portions over a four-hour period. The silver salts were filtered off and extracted with hot methanol and the combined filtrate and washings concentrated *in vacuo* to dryness. The dry reaction product was suspended in 70 ml. of methyl iodide and methylated again with the aid of 10 g. of silver oxide. After two more methylations in this manner 6.3 g. of crude crystalline product was isolated. Recrystallization from ethanol gave 4.8 g. (58%) of methyl 3-methyl-2,4:5,6-dimethylene-D-gluconate as long fine needles; m. p. 124–125°; $[\alpha]^{25}D$ −6.5° (*C*, 1.5; water).

Anal. Calcd. for $C_{10}H_{16}O_7$: C, 48.4; H, 6.5; OCH_3, 25.0. Found: C, 48.3; H, 6.5; OCH_3, 25.2.

Oxidation of the Saponified Acetolysis Product of Methyl 3-Methyl-2,4:5,6-dimethylene-D-gluconate.—A solution of 4.20 g. (0.017 mole) of methyl 3-methyl-2,4:5,-6-dimethylene-D-gluconate in 50 ml. of an acetolyzing mixture (35 ml. acetic anhydride, 15 ml. of acetic acid and 1 ml. of concentrated sulfuric acid) was allowed to remain at 0° for thirty minutes and then diluted with 400 ml. of ice water. The resulting solution was then neutralized with 75 g. of sodium bicarbonate, extracted with chloroform, and the dried chloroform solution concentrated *in vacuo* to a sirup (6.8 g.). This crude reaction product was presumed to be methyl 3-methyl-5-acetoxymethyl-6-acetyl-2,4-methylene-D-gluconate. The 6.8 g. of sirup was saponified at 60° with a solution of 11.30 g. (0.036 mole) of barium hydroxide octahydrate in 250 ml. of water. The barium salt was treated with the calculated amount of sulfuric acid and the barium sulfate that precipitated was removed by filtration. After concentrating the clear filtrate *in vacuo*, 2.2 g. of a nearly colorless sirup was obtained which presumedly was 3-methyl-2,4-methylene-D-gluconic acid.

For the oxidation all of the sirup was dissolved in a solution of 1.2 g. of potassium hydroxide in 50 ml. of water. The mixture was stirred and cooled to 5 to 10° and a solution of 5 g. of potassium permanganate in 90 ml. of water was introduced slowly over a thirty-minute period. Stirring was continued for thirty minutes after which the excess permanganate was destroyed with ethanol. The precipitated manganese dioxide was removed and washed with hot water by centrifugation. The supernatant solutions were combined and made slightly acid to litmus with sulfuric acid. The residue obtained by concentrating this solution *in vacuo* was suspended in 200 ml. of methanol and 3 ml. of concentrated sulfuric acid was added with stirring. Potassium sulfate precipitated and was removed and washed with methanol by centrifugation. The supernatant solution and washings were combined (500 ml.) and refluxed for ten hours. The sulfuric acid was then neutralized with barium carbonate, the barium sulfate removed, and the clear solution concentrated *in vacuo* to dryness. The residue was allowed to stand at 5 to 10° for two days with 200 ml. of methanol–ammonia. After concentrating this solution to dryness *in vacuo* the crude product was recrystallized twice from 80% ethanol. The yield of purified 3-methyl-2,4-methylene-xylotrihydroxyglutarodiamide was 0.3 g.; m. p. 305–306° (dec.); $[\alpha]^{25}D$ 0°. Jones and Wiggins[7] reported a melting point of 295° for this compound. An authentic sample prepared by their procedure[7] was found to melt at 305–306° (dec.).

Acknowledgment.—The authors are indebted to C. H. Van Etten of the Analytical and Physical Chemical Division of this Laboratory for performing the microanalyses.

Summary

A new methyl dimethylene gluconate has been isolated from the sublimate mixture obtained by heating methyl 2,4:3,5-dimethylene-D-gluconate *in vacuo* at 150°. The structure of the new diacetal has been shown to be methyl 2,4:5,6-dimethylene-D-gluconate. The rearrangement of a six-membered methylene acetal ring to a five-membered ring has thus been demonstrated.

The application of the procedure of Hudson and Hann and their associates[6] for the limited acetolysis of the methylene acetals of sugar alcohols to methyl 2,4:3,5-dimethylene-D-gluconate and methyl 2,4:5,6-dimethylene-D-gluconate has resulted in further confirmation of the relative stability of the 2,4-methylene acetal linkage to acetolysis.

PEORIA, ILLINOIS RECEIVED NOVEMBER 14, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY OF THE AMERICAN UNIVERSITY OF BEIRUT]

Sulfanilamide Derivatives Containing Urea, Thiourea or Hydrazide Groupings

BY EVA NIEMIEC[1]

Urea has been used in therapy along with sulfanilamides, its alleged effect being to counteract the action of *p*-aminobenzoic acid. It appeared of interest to prepare sulfanilamides containing urea or related groupings and study their bacteriostatic effects.

In the preparation of sulfanilamidourea (I) and sulfanilamidothiourea (II) from acetylsulfanilyl chloride and the appropriate semicarbazide hydrochloride (condensed in the presence of aqueous sodium acetate), deacetylation was accomplished by boiling for three hours in aqueous alcoholic hydrochloric acid solution. Alkaline hydrolysis causes liberation of ammonia; even ten hours of boiling with concentrated hydrochloric acid results only in partial hydrolysis.

(I) *p*-$H_2NC_6H_4SO_2NHNHCONH_2$
(II) *p*-$H_2NC_6H_4SO_2NHNHCSNH_2$
(III) *p*-$H_2NCH_2C_6H_4SO_2NHNHCONH_2$
(IV) *p*-$CH_3CONHC_6H_4SO_2NHNH_2$
(V) *p*-$CH_3CONHC_6H_4SO_2NHNHCOC_6H_5$
(VI) *p*-$CH_3CONHC_6H_4SO_2NHNHCOCH_3$
(VII) *p*-$CH_3CONHC_6H_4SO_2NHN(COCH_3)_2$
(VIII) *p*-$H_2NC_6H_4SO_2NHNH_2$

Marfanil or homosulfanilamide is interesting because its bacteriostatic action is not counteracted by *p*-aminobenzoic acid; its urea derivative (III) was prepared as above. Sulfanilylhydrazides should be available by either (1) treatment of acetylsulfanilyl chloride with the hydrazide, or (2) acylation of N^4-acetylsulfanilylhydrazine (IV), and hydrolysis at the N^4-position. Haslewood[2] prepared sulfanilylbenzhydrazide using the first method. Since acethydrazide is difficult to prepare, the second method was employed in this work. N^4-Acetylsulfanilylhydrazine[3] was prepared in good yield by grinding hydrazine dihydrochloride in a mortar with dry acetylsulfanilyl chloride and crystalline sodium carbonate.

If N^4-acetylsulfanilylhydrazine is treated in pyridine solution with one mole of benzoyl chloride, N^4-acetylsulfanilylbenzhydrazide[2] (V) is obtained; this yields sulfanilylbenzhydrazide on alkaline hydrolysis. Excess benzoyl chloride gives a product which appears to be a mixture of the mono- and dibenzhydrazide. This is in agreement with the experience of McFadyen and Stevens.[4] Acetylsulfanilylhydrazine in pyridine can be converted into either N^4-acetylsulfanilacethydrazide (VI) or the diacetate VII. When either product is subjected to acid hydrolysis[3] with 12 *N* hydrochloric acid or even with 6 *N* or 3 *N* hydrochloric acid, all acetyl groups are split off and only sulfanilylhydrazine[3] (III) is obtained.

Studies of the bacteriostatic properties of these compounds by Miss Aida Djanian at the Department of Bacteriology of this University indicate that sulfanilamidourea and 4-homosulfanilamidourea are superior to sulfathiazole in their inhibitory action upon *Clostridium welchii*, *Cl. tetani*, *Cl. sporogenes*, and *Cl. chauvei*. Sulfanilamidourea and sulfanilamidothiourea are approximately one-tenth as active against *Streptococcus viridans* as sulfathiazole, whereas homosulfanilamidourea has no inhibitory effect.

Experimental[5]

N^4-Acetylsulfanilamidourea.[6]—A mixture of 5 g. of semicarbazide hydrochloride, 10.5 g. of dry acetylsulfanilyl chloride, and 30 g. of crystalline sodium acetate is thoroughly ground in a mortar with a few cc. of water. The thick paste is then transferred with the minimum amount of water and heated for thirty minutes at 60°. After cooling the product is filtered, washed, and crystallized from boiling water, in which it is not very soluble; needles, m. p. 223–224° with decomposition, yield 6 g.

(1) Part of a Master's thesis submitted to the American University of Beirut, 1946.

(2) Haslewood, *Biochem. J.*, **35**, 1307 (1941).

(3) Curtius and Stoll, *J. prakt. Chem.*, **112**, 1117 (1926).

(4) Compare McFadyen and Stevens, *J. Chem. Soc.*, p. 584 (1936).

(5) All melting points are uncorrected.

(6) After the completion of these experiments, Roth and Degering, THIS JOURNAL, **67**, 126 (1945), reported the preparation of this compound in comparable yield in pyridine solution