air, but also turned dark red in the solvent upon standing in the ice box.

Anal. Calcd. for $C_{10}H_{11}O_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.95; H, 6.05; N, 7.78.

β-Amino-α-(5-benzyloxy-3-indole)propanol (XX). 5-Benzyloxytryptophan (9 g.) was added portionwise to a stirred and refluxing mixture of 5 g. of lithium aluminum hydride in 500 ml. of dry ether during a 2-hr. period. The heating and stirring was continued for another 3 hr. and the mixture was allowed to stand overnight. The excess lithium aluminum hydride was carefully decomposed with 10 ml. of ethyl acetate and 200 ml. of 20% aqueous sodium potassium tartarate solution was then slowly added to the reaction mixture with stirring. The ether layer was separated and the water layer was extracted twice with small portions of ether. The combined ether solutions were washed with dilute sodium bicarbonate solution, water, and then dried over magnesium sulfate. Evaporation of the ether left 5.3 g. (61%) of a slightly reddish oil which soon solidified, m.p. 106–108°. It was recrystallized from benzene to give colorless small needles, m.p. 108–109°.

Anal. Calcd. for $C_{18}H_{20}N_2O_2$: N, 9.45. Found: N, 9.26.

N,N'-bis-(5-benzyloxyskatyl)piperazine (XXI). A solution of 7 g. of 5-benzyloxygramine and 0.9 g. of piperazine in 300 ml. of toluene was refluxed with stirring under nitrogen for 24 hr. Some of the product began to precipitate after a few hours. Filtration of the hot reaction mixture yielded 5.5 g. (80%) of the compound melting at 229–230°. Crystallization from dimethylformamide did not change this melting point.

Anal. Calcd. for $C_{36}H_{36}N_4O_2$: N, 10.07. Found: N, 10.01.

5-Benzyloxy-2-carbethoxy-3-indolecarboxaldehyde (XXIII). A mixture of 8 g. of *N*-methylformanilide and 9 g. of phosphoryl chloride was stirred for 15 min. under anhydrous conditions. Forty g. of ethylene dichloride was added to the mixture, followed by 14.2 g. of ethyl 5-benzyloxy-2-indolecarboxylate.[14] After stirring and refluxing for 1 hr. the reaction mixture was poured into a solution of 40 g. of sodium acetate in 80 ml. of ice water with stirring. The yellow paste which separated was triturated twice with water and once with ether to yield a finely divided solid, weighing 15 g. (96%), m.p. 240–242°. A pure sample was obtained by recrystallization of the crude material from ethylene dichloride to give light yellow, fine needles, m.p. 244–245°.

Anal. Calcd. for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33. Found: C, 71.03; H, 5.25; N, 4.43.

The *oxime* was obtained by the following procedure: A mixture of 3 g. of indole aldehyde, 3 g. of hydroxylamine hydrochloride in 15 ml. of pyridine, and 15 ml. of absolute ethanol was heated gently on a steam bath for 2 hr. The excess solvent was evaporated and the residue was treated with cold water. The crude product was recrystallized from dilute ethanol to give 2.6 g. (83%) of colorless prisms, m.p. 220–221°.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: N, 8.28. Found: N, 8.12.

The *2,4-dinitrophenylhydrazone* was prepared in the usual manner and was recrystallized from ethyl acetate–ethanol to give a bright red material in almost theoretical yield, m.p. 278–280°.

Anal. Calcd. for $C_{25}H_{21}N_5O_7$: N, 13.91. Found: N, 13.63.

β-(2-Carbethoxy-5-benzyloxy-3-indole)acrylic acid (XXIV). Ten drops of piperidine was added to a solution of 1.5 g. of indole aldehyde (XXIII) and 3 g. of malonic acid in 15 ml. of pyridine. The solution was heated on a steam bath at 50–70° for 80 hr., then poured into ice water and acidified with dilute hydrochloric acid. The precipitate was filtered off and treated with 10% sodium hydroxide solution. The resulting insoluble material was filtered off and the filtrate was again acidified. The precipitate was recrystallized from 90% ethanol to yield 0.56 g. (31%) of pale yellow, cottony needles, m.p. 230° dec.

Anal. Calcd. for $C_{21}H_{19}NO_5$: C, 69.03; H, 5.24; N, 3.83. Found: C, 68.65; H, 5.15; N, 3.64.

PHILADELPHIA 44, PA.

[CONTRIBUTION FROM THE "LABORATORIO DE QUÍMICA BIOLÓGICA," FACULTAD DE CIENCIAS MÉDICAS, AND THE "LABORATORIOS DE INVESTIGACIÓN," E. R. SQUIBB & SONS ARGENTINA S.A.]

Reaction of Ammonia with Some Acetylated and Benzoylated Monosaccharides. VI. Derivatives of L-Arabinose, D-Xylose, and D-Ribose

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The tetraacetylated and tetrabenzoylated derivatives of L-arabinose, D-xylose and D-ribose gave, on treatment with methanolic ammonia, the *N,N'*-diacyl-pentosylidenediamines. By ammonolysis of tetrabenzoyl-L-arabononitrile and of tetrabenzoyl-D-xylononitrile, the *N,N'*-dibenzoyltetrosylidenediamines were obtained.

In our first papers[1] we described the action of methanolic ammonia on the pentaacetyl- and pentabenzoylhexoses, a reaction that leads, with opening of the pyranose or furanose ring, to the production as principal products, of the open chain *N,N'*-diacetyl-(I) or *N,N'*dibenzoylhexosylidenediamines (II). The reaction was afterwards applied to tetraacetyl and tetrabenzoyl-L-rhamnopyranose.[2] The products and yields almost duplicated the results with the corresponding D-mannose derivatives; while tetraacetyl-L-rhamnose produced only *N,N'*-diacetyl-L-rhamnosylidenediamine (III), tetrabenzoyl-L-rhamnose gave, as happened with pentabenzoyl-D-mannose, two products; the principal one was the open chain compound, *N,N'*-dibenzoyl-L-rhamnosylidenediamine (IV) and the secondary compound was a cyclic pyranose derivative, *N*-benzoyl-L-rhamnopyranosylamine.

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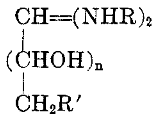
[1] V. Deulofeu and J. O. Deferrari, *J. Org. Chem.*, **17**, 1087, 1093, 1097 (1952).

[2] J. O. Deferrari and V. Deulofeu, *J. Org. Chem.*, 22, 802 (1957).



$$\begin{array}{l} CH{=}(NHR)_2 \\ \quad | \\ (CHOH)_n \\ \quad | \\ CH_2R' \end{array}$$

(I) $n = 4; R = CH_3CO; R' = OH$
(II) $n = 4; R = C_6H_5CO; R' = OH$
(III) $n = 4; R = CH_3CO; R' = H$
(IV) $n = 4; R = C_6H_5CO; R' = H$
(V) $n = 3; R = CH_3CO; R' = OH$
(VI) $n = 3; R = C_6H_5CO; R' = OH$
(VII) $n = 2$ (L-erythro); $R = C_6H_5CO; R' = OH$
(VIII) $n = 2$ (D-threo); $R = C_6H_5CO; R' = OH$

We have extended this study to the pentoses. Experiments with D-lyxose have already been reported.[3] In this paper, the results of the ammonolysis of the tetraacetyl- and tetrabenzoyl- derivatives of L-arabinose, D-xylose and D-ribose are described.

All of the tetraacetylpentoses gave the open chain, *N*,*N'*-diacetylpentosylidenediamines (V). No crystalline compound could be isolated by the ammonolysis of tetraacetyl-D-xylopyranose. an experience in agreement with the results of Hockett and Chandler[4] who also could not obtain a definite product by the ammonolysis of tetraacetyl-*aldehydo*-D-xylose.

The tetrabenzoylpentoses produced the expected *N*,*N'*-dibenzoylpentosylidenediamines (VI). The isomeric *N*,*N'*-dibenzoyl-D-arabinosylidenediamine was obtained by ammonolysis with methanolic ammonia of the pentabenzoyl-D-glucononitrile and the racemic *N*,*N'*-dibenzoyl-DL-arabinosylidendiamine and its tetraacetyl derivative were prepared. As in the case of the ammonolysis of the pentabenzoyl-D-galactononitrile,[3] when methanolic ammonia was employed, the benzoyl esterifying the primary hydroxyl was eliminated, while Restelli de Labriola and Duelofeu[5] using ethanolic ammonia obtained 5-*O*-benzoyl-*N*,*N'*-dibenzoyl-D-arabinosylidenediamine. This compound loses easily the primary benzoyl under the action of methanolic ammonia. As will be described in a further publication, this difference in activity depends not only on the higher concentration of the ammonia in methanol, but on the alcohol itself, methanol being more active as a solvent than ethanol.

With a few exceptions, the yields of the *N*,*N'*-diacylpentosylidenediamines were of the same order as those from the acylated compounds of the hexose series. These results, taken together with those obtained in the ammonolysis of the tetraacetyl-L-rhamnose and tetrabenzoyl-L-rhamnose[2] are interesting, because the *N*,*N'*-diacyldiamines of the monosaccharides (I–VI) are formed by an intramolecular mechanism[6] and for the case of the acylated pentoses and L-rhamnose, only three acyl groups can participate in it. The acyl group at carbon atom 1 does not play any important role in the reaction.[1]

In this paper, the ammonolysis of tetrabenzoyl-L-arabononitrile and of tetrabenzoyl-D-xylononitrile is also reported. Neither of these compounds could be obtained in a crystalline condition, although the analytical figures for the cyano group were indicative of a rather high purity.[7] Ammonolysis gave the expected *N*,*N'*-dibenzoyl-L-erythrosylidenediamine (VII) from the first nitrile and *N*,*N'*-dibenzoyl-D-threosylidenediamine (VIII) from the second.

EXPERIMENTAL

The methanolic ammonia employed was of 16% concentration. Melting points are uncorrected.

N,N-Diacetyl-L-*arabinosylidenediamine.* Tetraacetyl-α-L-arabopyranose[8] (5 g.) was dissolved in 150 ml. methanolic ammonia, and the solution after staying 24 hr. at room temperature, evaporated in vacuum. The remaining sirup was well dried, extracted three times with 20 ml. ethyl acetate, and dissolved in 25 ml. absolute ethanol. By scratching, crystals appeared and after standing overnight in the cold room, they were filtered and washed well with small amounts of boiling methanol, to get rid of an amorphous product that contaminated them. Yield: 310 mg. (7.9%) m.p. 193–194°. Recrystallized several times from methanol (Darco) the m.p. was 193–194°; $(\alpha)_D^{18°}$ +8.8°, (H_2O) Isbell and Frush[6] give m.p. 189–191°; $[\alpha]_D^{20°}$ +9.79°.

N,N'-Dibenzoyl-L-*arabinosylidenediamine.* The tetrabenzoyl-β-L-arabopyranose[9] (15 g.), was shaken to dissolution with 450 ml. methanolic ammonia, the solution left 24 hr. at room temperature, and evaporated to dryness in vacuum. The crystalline residue was suspended in ethanol, filtered, and washed well with the same solvent. 2.98 Grams of crystals were obtained, m.p. 192–195° and from the mother liquors, another 540 mg. were collected, giving a total yield of 35.6%. Recrystallized several times from ethanol, long needles melting 197–198°; $[\alpha]_D^{30°}$ −5.2° (*c*, 1.2; pyridine).

Anal. Calcd. for $C_{19}H_{22}N_2O_6$: C, 60.96; H, 5.88. Found: C, 61.24; H, 6.08.

N,N'-Dibenzoyl-D-*arabinosylidenediamine.* (a) *From pentabenzoyl*-D-*glucononitrile.* The pentabenzoyl-D-glucononitrile, finely ground, (15 g.) was dissolved, by shaking, in 450 ml. methanolic ammonia. After 24 hr. at room temperature the solution was evaporated in vacuum. The crystalline residue was suspended in cold ethanol, filtered, washed with the same solvent, and dried. Yield 2.97 g., m.p. 192–195°. From the mother liquors, after drying and extracting the benzamide with ethyl acetate, a further 390 mg. were isolated, m.p. 197–198° (total yield 42%). After several recrystallizations from methanol the product melted 198–199°; $[\alpha]_D^{31°}$ +5.1.

Anal. Calcd. for $C_{19}H_{22}N_2O_6$: C, 60.96; H, 5.88. Found: C, 60.67; H, 5.88.

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(3) V. Deulofeu and J. O. Deferrari, *Anais acad. brasil. cienc.*, **26**, 69 (1954). V. Deulofeu, J. O. Deferrari, and E. Recondo, *Anales asoc. quim. arg.*, **46**, 137 (1958).

(4) R. C. Hockett and L. R. Chandler, *J. Am. Chem. Soc.*, **66**, 957 (1944).

(5) E. Restelli de Labriola and V. Deulofeu, *J. Org. Chem.*, 12, 726 (1947).

(6) H. S. Isbell and H. L. Frush, *J. Am. Chem. Soc.*, **71**, 1579 (1949); V. Deulofeu and J. O. Deferrari, *Anales asoc. quim. arg.*, **38**, 241 (1950); R. C. Hockett, V. Deulofeu, and J. O. Deferrari, *J. Am. Chem. Soc.*, **82**, 1840 (1950).

(7) The determination of the nitrile group was made according to B. G. Berinzaghi, *Anales asoc. quim. arg.*, **44**, 120 (1956).

(8) R. E. Deriaz, W. G. Overend, M. Stacey, E. G. Teece, and L. F. Wiggins, *J. Chem. Soc.*, 1879 (1949).

(9) H. G. Fletcher and C. S. Hudson, *J. Am. Chem. Soc.*, **69**, 1145 (1947).

(*b*) *From 5-O-benzoyl-N,N′-dibenzoyl-*D*-arabinosylidenediamine.* One gram of 5-*O*-benzoyl-*N,N′*-dibenzoyl-D-arabinosylidenediamine was dissolved in 30 ml. methanolic ammonia and the solution worked as described above. *N,N′*-Dibenzoyl-D-arabinosylidenediamine (695 mg.) melting 196–197° $[\alpha]_D^{20°}$ +4.90°, were obtained. No depression was observed when mixed with the product prepared under (a).

*N,N-Dibenzoyl-*DL*-arabinosylidenediamine.* When 200 mg. of each isomer was dissolved in 10 ml. of boiling ethanol, the solution, on cooling, yielded fine needles melting 192°. The melting point was not increased by recrystallization $[\alpha]_D$ ±0.0°.

*Tetra-O-acetyl-N,N′-dibenzoyl-*L*-arabinosylidenediamine.* One gram of *N,N′*-dibenzoyl-L-arabinosylidenediamine was dissolved with gentle heating in 34 ml. of a mixture (1:1) of pyridine and acetic anhydride. After 24 hr. at room temperature, the solution was poured into 200 ml. of ice water when a precipitated formed, which crystallized very easily. Next day the crystals were filtered, washed, and dried to yield 1.18 g. of long prisms, melting at 138–140°. From the mother solution, after extracting with chloroform and processing the extract in the usual way, another 250 mg. were obtained; m.p. 141–142°. Total yield 98%. Recrystallized several times from ethanol, long prisms melting 143–145°; $[\alpha]_D^{16°}$ −73.3° (*c*, 0.74, chloroform).

Anal. Calcd. for $C_{27}H_{30}N_2O_{10}$: C, 59.80; H, 5.54. Found: C, 59.88; H, 5.49.

*Tetra-O-acetyl-N,N′-dibenzoyl-*D*-arabinosylidenediamine* was obtained in a similar way from the D-isomer. M.p. 144–145°, $[\alpha]_D^{17°}$ +73.4°.

Anal. Calcd. for $C_{27}H_{30}N_2O_{10}$: C, 59.80; H, 5.54. Found: C, 59.84; H, 5.67.

*Tetra-O-acetyl-N,N′-dibenzoyl-*DL*-arabinosylidenediamine.* A mixture of 100 mg. of each isomer was dissolved in 0.6 ml. of boiling ethanol. By cooling, 91 mg. of crystals melting 168–170° were obtained. The melting point remained constant by further recrystallization, $[\alpha]_D^{17°}$ ±0.0°.

*Tetra-O-benzoyl-N,N′-dibenzoyl-*D*-arabinosylidenediamine.* Five hundred milligrams of *N,N′*-dibenzoyl-D-arabinosylidenediamine were dissolved by gently heating in 6.25 ml. dry pyridine. The solution was cooled at room temperature and 1.25 ml. benzoyl chloride added. It was then heated 10 min. at 60° and left at room temperature overnight. Next day the suspension was poured into ice water and a sirup precipitated. After washing well with water, the sirup was dried in a desiccator and treated with ligroin, when it gave a solid. It was crystallized by dissolving in small amounts of benzene, adding ethyl ether to turbidity, and left standing at room temperature. Small needles, that after several recrystallizations melted 134–135°, when dried at 100° vacuum. Lower m.p. were obtained when the product was not well dried. $[\alpha]_D^{28°}$ +62.5° (*c*, 0.98, chloroform).

Anal. Calcd. for $C_{47}H_{38}N_2O_{10}$: C, 71.39; H, 4.81; N, 3.54. Found: C, 71.80; H, 4.75; N, 3.07.

L*-Arabinose diphenylhydrazone.* The alcoholic mother liquors from the preparation of *N,N′*-dibenzoyl-L-arabinosylidenediamine were evaporated to a sirup, which was extracted with ethyl acetate to eliminate the benzamide. The insoluble was dissolved in 6 ml. water and treated with 185 mg. anhydrous solid acetate and 750 mg. diphenylhydrazine hydrochloride. The solution was heated 30 min. at 75° and left standing. Crystals appeared that, after 72 hr., were filtered and washed with ethanol. L-Arabinose diphenylhydrazone (123 mg.), m.p. 195°, were collected. Identified by mixed m.p.

*N,N′-Diacetyl-*D*-ribosylidenediamine.* Tetraacetyl-β-D-ribose[10] (1.5 g.), was dissolved in 45 ml. methanolic ammonia. After standing 24 hr. at room temperature, the solution was evaporated to dryness in vacuum. The well dried residue was extracted several times with ethyl acetate, dried again, dissolved in 4 ml. absolute ethanol and evaporated slowly at room temperature. Crystals appeared after several days, that increased by scratching. They were filtered and washed well with absolute ethanol. M.p. 123–126°. Yield 150 mg. By concentration of the mother liquors 150 mg. more were obtained (m.p. 122–125°). Total yield 300 mg. (25%).

When recrystallized from boiling ethanol long needles melting 124–126° were obtained. After drying 3 hr. at 100° over phosphorus pentoxide they melted 154–155°. $[\alpha]_D^{24°}$ +14.7° (*c*, 0.68, H_2O).

Anal. Calcd. for $C_9H_{18}N_2O_6$: C, 43.20; H, 7.20; N, 11.20. Found: C, 42.90; H, 7.14; N, 10.99.

*Tetra-O-acetyl-N,N′-diacetyl-*D*-ribosylidenediamine. N,N′*-Diacetyl-D-ribosylidenediamine (50 mg.) was heated to dissolution with 1.5 ml. of a mixture of pyridine and acetic anhydride (1:1). After 24 hr. standing at room temperature, the solution was evaporated in a desiccator, when 79 mg. of crystals were obtained, melting at 175–176°. Recrystallized from ethanol prisms melting 184–185°. $[\alpha]_D^{20°}$ +18.5 (*c*, 0.54, chloroform).

Anal. Calcd. for $C_{17}H_{26}N_2O_{10}$: C, 48.69; H, 6.31; N, 6.69. Found: C, 49.58; H, 6.18; N, 6.65.

*N,N-Dibenzoyl-*D*-ribosylidenediamine.* Three grams of tetrabenzoyl-β-D-ribopyranose[11] were dissolved, by shaking, in 110 ml. of methanolic ammonia. After 18 hr. standing at room temperature, the solution was evaporated in vacuum to dryness. The residue was well extracted with ethyl acetate and the remaining solid recrystallized from water. It yielded 640 mg. of crystals (35%) melting 185–187°. For analysis it was recrystallized from water. M.p. 190°; $[\alpha]_D^{26°}$ −7.3° (*c*, 1.0, pyridine).

Anal. Calcd. for $C_{19}H_{22}N_2O_6$: C, 60.95; H, 5.92; N, 7.48. Found: C, 61.13; H, 6.02; N, 7.60.

*Tetra-O-acetyl-N,N′-dibenzoyl-*D*-ribosylidenediamine.* Four hundred mg. of *N,N′*-dibenzoyl-D-ribosylidenediamine were suspended in a mixture of 9 ml. (1:1) of pyridine and acetic anhydride. The suspension was gently heated to dissolution and after 16 hr. standing at room temperature, it was poured into ice water. A sirup precipitated that crystallized very easily, by washing with cold water. The crystals were filtered and recrystallized from ethanol-water. M.p. 172–173°; $[\alpha]_D^{24°}$ −10.4° (*c*, 1.1; chloroform).

Anal. Calcd. for $C_{27}H_{30}N_2O_{10}$: C, 59.77; H, 5.57; N, 5.16. Found: C, 59.64; H, 5.69; N, 5.06.

*Tetrabenzoyl-α-*D*-xylopyranose.* The following modification of the procedure of Fletcher and Hudson[12] was employed. Five grams of finely powdered D-xylose were well suspended in 30 ml. pyridine, cooled at 0°, and 24 ml. of benzoyl chloride slowly added, maintaining the temperature at 0–5°. After 2 hr. at 0°, the reaction mass was left 24 hr. at room temperature. Chloroform (150 ml.) was then added and the solution poured into chopped ice. The chloroform layer was decanted and washed twice with 3*N* sulfuric acid, with saturated sodium hydrogen carbonate solution, and with water. After drying and passing through a layer of Darco the chloroform was evaporated, leaving a sirup that when washed and scratched several times with small portions of ligroin, crystallized. The crude product was recrystallized from ethanol, when 13–14 g. (yield 71%) of large prisms melting 114–116° were obtained. After recrystallizing several times from ethanol, they melted 116–117°; $[\alpha]_D^{30°}$ +148.7 (*c*, 1.16, chloroform). Fletcher and Hudson[12] give 119–120°: $[\alpha]_D^{20°}$ +149.5°.

Anal. Calcd. for $C_{33}H_{26}O_9$: C, 69.80; H, 4.58. Found: C, 69.56; H, 4.81.

*N,N′-Dibenzoyl-*D*-xylosylidenediamine.* Finely ground tetrabenzoyl-α-D-xylopyranose (12.4 g.) was dissolved in 315 ml. of methanolic ammonia and left 48 hr. at room tem-

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[10] P. A. Levene and R. St. Tipson, *J Biol Chem.*, **92**, 109 (1931).

[11] J. Jeanloz, H. G. Fletcher, and C. S. Hudson, *J. Am. Chem. Soc.*, **70**, 4052 (1948).

[12] H. G. Fletcher and C. S. Hudson, *J. Am. Chem. Soc.*, **69**, 921 (1947).

perature. The solution was then evaporated in vacuum and the residual syrup dissolved in 60 ml. ethanol. By keeping at room temperature for a few days, crystals appeared, which were filtered and washed with ethanol. 2.43 Grams of needles, m.p. 182–184°, were collected (yield 30%). Recrystallized once from water and three times from ethanol, they melted 184–185°, $[\alpha]^{22°}_{\mathrm{D}}$ −2.2° (*c*, 1.4, pyridine).

Anal. Calcd. for $C_{19}H_{22}N_2O_6$: C, 60.96; H, 5.88. Found: C, 60.95; H, 6.09.

*Tetra-O-acetyl-N,N′-dibenzoyl-*D*-xylosylidenediamine.* The *N,N′*-dibenzoyl-D-xylosylidenediamine (1 g.) was acetylated with pyridine–acetic anhydride. Yield: 1.25 g. (86%) of crystals melting 178–179°. Recrystallized from ethanol, long prisms melting at 179°; $[\alpha]^{22°}_{\mathrm{D}}$ −50.4° (*c*, 0.95, chloroform).

Anal. Calcd. for $C_{27}H_{30}N_2O_{10}$: C, 59.80; H, 5.54; N, 5.16. Found: C, 59.57; H, 5.55; N, 5.13.

*Tetrabenzoyl-*L*-arabonitrile.* Three grams of L-arabinose oxime were suspended in 18 ml. dried pyridine and 18 ml. of benzoyl chloride added, in such a way that the temperature of the suspension was maintained at 95–100°. The oxime dissolved and a solid precipitated. After keeping the suspension at room temperature for 16 hr., it was poured into ice water. The pasty sirup that precipitated was ground many times with fresh water and dried in a desiccator. When treated with cold methanol it became solid. It was dissolved by boiling in the same solvent, a small amount of Darco added, and after filtering, the solution was slowly cooled, when an amorphous solid precipitated. Repetition of the procedure several times, gave a noncrystalline solid that melted 90–94°. Yield 7.2 g. (70%).

For further purification, 500 mg. of the nitrile were dissolved in the smallest volume of benzene and passed through a column of 16 g. alumina, acid washed, grade I–II. After washing the column with 15 ml. benzene, the nitrile was eluted with benzene with 1% methanol, fractions of 5–7 ml. being collected. Evaporation of fractions 3–11 gave 350 mg. of a solid that was dissolved several times in boiling methanol and recovered by cooling. It was amorphous, melted 107–108°, with sintering from 94° (after drying at 76° in vacuum); $[\alpha]^{25°}_{\mathrm{D}}$ −16.5° (*c*, 1.2; chloroform). The constants were not appreciably changed by further dissolution and precipitation. It could not be obtained crystalline by employing other solvents. High vacuum distillation also failed.

Anal. Calcd. for $C_{33}H_{25}NO_8$: C, 70.33; H, 4.47; N, 2.49; CN, 4.62. Found: C, 70.53; H, 4.45; N, 2.59; CN, 4.42.

*N,N′-Dibenzoyl-*L*-erythrosylidenediamine.* Two grams of the amorphous tetrabenzoyl-L-arabonitrile, melting 92–94°, were suspended in 50 ml. methanolic ammonia, dissolved by agitation, and left 18 hr. standing at room temperature. The solution was evaporated in vacuum to dryness and the dark yellow residue suspended in ethanol and filtered. Washing with ethanol was continued, until the solid was almost white. It was recrystallized from 90% ethanol, when 230 mg. (19%) of long prisms, melting 218°, were obtained. For analysis it was recrystallized several times from 90% ethanol. M.p. 220°, $[\alpha]^{27°}_{\mathrm{D}}$ +13.1° (*c*, 0.34, pyridine).

Anal. Calcd. for $C_{18}H_{20}N_2O_5$: C, 62.78; H, 5.57; N, 8.14. Found: C, 62.98; H, 5.94; N, 8.22.

*Triacetyl-N,N′-dibenzoyl-*L*-erythrosylidenediamine.* Two hundred milligrams of N,N′-dibenzoyl-L-erythrosylidenediamine were acetylated with pyridine–acetic anhydride. Needles, from absolute ethanol, m.p. 183–184°, formed. $(\alpha)^{27°}_{\mathrm{D}}$ +8.9 (*c*, 1.0, chloroform).

Anal. Calcd. for $C_{24}H_{26}N_2O_8$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.49; H, 5.44; N, 5.97.

*Tetrabenzoyl-*D*-xylononitrile.* To a suspension in 54 ml. of dry pyridine, of the siruppy D-xylose oxime obtained from 9 g. of D-xylose, 45 ml. of benzoyl chloride were added, keeping the temperature between 95–100°. The red-brown suspension obtained was left at room temperature for 16 hr., poured into ice water and the sirup that precipitated, washed well with water and dried in a desiccator. By treatment with different solvents, it did not solidify. It was then dissolved in the minimum amount of cold benzene. The red solution obtained was washed well with 2*N* hydrochloric acid, with saturated solution of sodium hydrogen carbonate and with water. It was dried and chromatographed on alumina, acid washed, grade II, eluting with benzene. By evaporation of the middle eluted fractions, a solid was recovered (yield: 21 g.), which when chromatographed again, gave a product sintering at 49° and melting 61–66°; $[\alpha]^{24°}_{\mathrm{D}}$ = −2.9 (*c*, 4.6; chloroform). Repetition of the chromatography did not change the constants. By chromatography on Magnesol or silica gel, no improvements were observed. Although impure, it contained an appreciable amount of nitrile.

Anal. Calcd. for $C_{35}H_{25}NO_8$: CN, 4.62%. Found: 4.12%.

*N,N′-Dibenzoyl-*D*-threosylidenediamine.* Five grams of the tetraacetyl-D-xylononitrile, purified by chromatography on alumina, were treated in the usual way with 125 ml. of methanolic ammonia. After standing 18 hr. at room temperature, the solution was evaporated in vacuum to dryness and the residue treated with 15 ml. of cold absolute ethanol. On standing at 0° it gave 560 mg. of fine needles (yield 18.3%), melting 184°. By recrystallization from 95% ethanol a m.p. 189–190° was obtained. $[\alpha]^{27°}_{\mathrm{D}}$ +1.7° (*c*, 0.97; pyridine); $[\alpha]^{24°}_{\mathrm{D}}$ −4.9° (*c*, 0.93; ethanol:water; 3:1).

Anal. Calcd. for $C_{18}H_{20}N_2O_5$: C, 62.78; H, 5.57; N, 8.14. Found: C, 62.90; H, 5.72; N, 7.97.

*Triacetyl-N,N′-dibenzoyl-*D*-threosylidenediamine.* Four hundred milligrams of *N,N′*-dibenzoyl-D-threosylidenediamine were acetylated in the usual way with pyridine–acetic anhydride and worked in the usual way. Recrystallized from ethanol 95%, it gave needles m.p. 183–184°; $[\alpha]^{27°}_{\mathrm{D}}$ +79.3° (*c*, 1.2, chloroform).

Anal. Calcd. for $C_{24}H_{26}N_2O_8$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.32; H, 5.39; N, 6.17.

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