

and 30 ml. of triethylamine was allowed to stand overnight at room temperature. After filtering from amine hydrobromide and evaporating under reduced pressure, the residue was taken up in ethanol. Slow evaporation over several days gave light yellow crystals of m.p. 82.5–86.5°, yield 50%; recrystallized from ethanol, m.p. 91–92° (B. and R.³² 87.5°); it gave no mixture m.p. depression with a sample prepared by the Barnes procedure³² from the β -methoxy compound above.

Anal. Calcd. for $C_{19}H_{19}BrO_2$: C, 63.52; H, 5.33. Found: C, 63.22; H, 5.20.

Attempts to prepare *cis* isomers in the 2',4',6'-trimethylchalcone (benzalacetomesitylene) series by exposure of

benzene solutions of *trans* isomers to sunlight for 2.5 hr., for 4 days or for 15 days, gave only starting compound and resins.

p-Anisylmesitylacetylene was prepared by dehydrobromination of *trans*- α -bromo-4-methoxybenzalacetomesitylene (m.p. 91–92°) by the Bickel procedure³³ except that a threefold reaction time was necessary; recrystallized from ethanol, m.p. 66.5–67° (colorless).

Anal. Calcd. for $C_{19}H_{19}O_2$: C, 81.99; H, 6.52. Found: C, 81.58; H, 6.54.

(33) C. L. Bickel, *THIS JOURNAL*, **69**, 2134 (1947).

CHARLOTTESVILLE, VA.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CHEMICAL DIVISION, MERCK & CO., INC.]

Synthesis of DL-Dimethyldihydro- α -lipoic Acid

BY ARTHUR F. WAGNER, EDWARD WALTON, CARL H. HOFFMAN, LOUIS H. PETERSON, FREDERICK W. HOLLY AND KARL FOLKERS

RECEIVED MARCH 10, 1955

DL-Dimethyldihydro- α -lipoic acid has been synthesized. It showed no α -lipoic acid activity in the enzymatic POF assay. Attempts to convert this acid to DL- α -lipoic acid gave only low yields of α -lipoic acid as determined by enzymatic assay.

Several syntheses of DL- α -lipoic acid (XI) have been reported.¹ A preliminary account of the synthesis of (+)-, (–)- and DL- α -lipoic acid has been reported from these laboratories.² This paper describes a synthesis of DL-dimethyldihydro- α -lipoic acid (X). Demethylation of this acid gave only low yields of α -lipoic acid as determined by the enzymatic POF assay.³

γ -Butyrolactone (I) was converted to 2,4-dibromobutyric acid (II).⁴ The first sulfur-containing intermediate of this sequence, 2,4-di-(methylthio)-butyric acid (III), was prepared by adding 2,4-dibromobutyric acid (II) to an excess of sodium methyl mercaptide in methanol solution. Although syntheses of the 2,4-dihalo-butyric acids are described in the literature,^{4,5} preparation of the pure acids was complicated by the ready elimination of the 4-halogen to give mixtures of the dihalo acid and the corresponding α -halo- γ -butyrolactone. Consequently, the crude bromination mixtures were treated immediately with the sodium mercaptide. The dithioether was purified by distillation, although the undistilled product was sufficiently pure for use in the next step.

A second synthesis of this dithioether, involving the addition of an alkyl mercaptide to a substituted γ -butyrolactone,⁴ gave lower yields. α -Methylthio- γ -butyrolactone was prepared from sodium methyl mercaptide and α -bromo- γ -butyrolactone. A toluene suspension of sodium methyl mercaptide

reacted with α -methylthio- γ -butyrolactone to yield an intermediate addition product. Fusion of this product at 165–170° for one hour yielded the sodium salt of 2,4-di-(methylthio)-butyric acid. The yields from this alternate method were one-half those of the direct method.

2,4-Di-(methylthio)-butyric acid was converted to 2,4-di-(methylthio)-butyryl chloride (IV) which was purified by distillation and characterized by conversion to the methyl ester.

The acylation of ethyl *t*-butyl α -ethoxymagnesiummalonate with 2,4-di-(methylthio)-butyryl chloride yielded the intermediate, ethyl *t*-butyl [2,4-di-(methylthio)-butyryl]-malonate (V). This product was not isolated but was converted to the β -keto ester VI by elimination of the *t*-butyl group and decarboxylation⁶ using catalytic amounts of *p*-toluenesulfonic acid in refluxing benzene solution. Ethyl [2,4-di-(methylthio)-butyryl]-acetate (VI) was purified by distillation and showed ultraviolet absorption characteristic of α -keto thioethers.⁷ Absorption maxima were observed at 246 and 294 m μ .

The β -keto ester VI was converted to methyl 4-carbethoxy-4-[2,4-di-(methylthio)-butyryl]-butyrate (VII) by either a condensation with methyl acrylate or alkylation with methyl β -chloropropionate. The product VII distilled as a viscous high-boiling oil and showed ultraviolet absorption maxima characteristic of α -keto thioethers.⁷ Hydrolysis and decarboxylation of the keto diester VII with hydrochloric acid in glacial acetic acid solution was not complete. Although the acidic product gave the calculated neutralization equivalent for acid VIII, extra carbonyl absorption was noted in the infrared. The crude product was saponified with cold 1 *N* sodium hydroxide. After acidification and extraction a semi-solid mixture was obtained. Fusion of this mixture at 80–85° for one hour completed the decarboxylation to yield 4-

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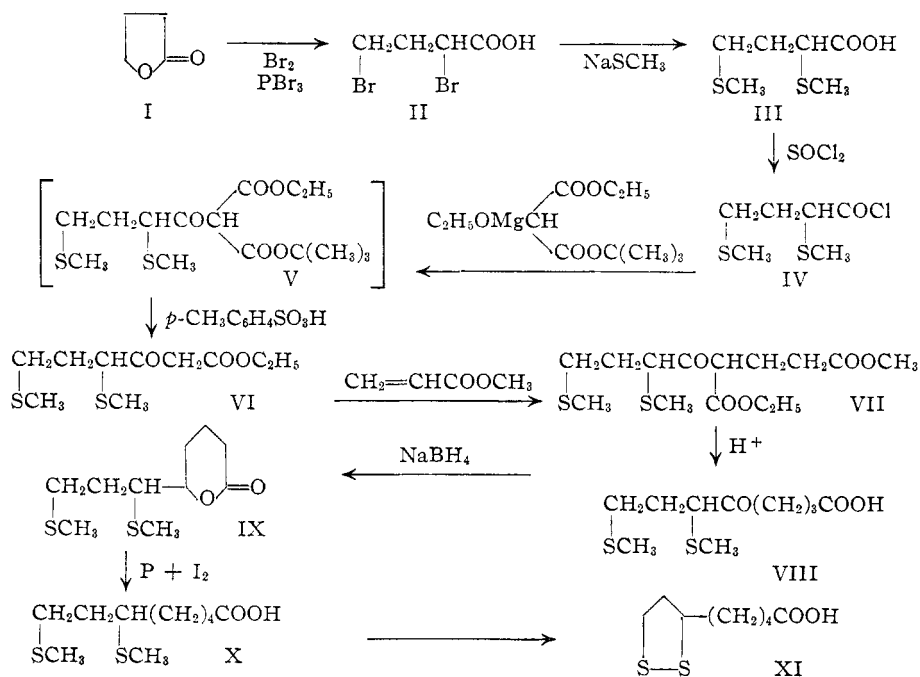
(3) I. C. Gunsalus, M. I. Dolin and L. Struglia, *J. Biol. Chem.*, **194**, 849 (1952).

(4) H. Plieninger, *Ber.*, **83**, 265 (1950).

(5) J. E. Livak, E. C. Britton, J. C. Vander Weele and M. F. Murray, *THIS JOURNAL*, **67**, 2218 (1945); E. C. Britton and J. C. Vander Weele, U. S. Patent 2,530,348 (1950); E. C. Britton, J. C. Vander Weele and J. E. Livak, U. S. Patent 2,557,779 (1951).

(6) D. S. Breslow, E. Baumgarten and C. R. Hauser, *THIS JOURNAL*, **66**, 1286 (1944).

(7) E. A. Fehnel and M. Carmack, *ibid.*, **71**, 84 (1949).



[2,4-di-(methylthio)-butyryl]-butyric acid (VIII). Infrared and ultraviolet spectra were consistent with the structure VIII.

Wolff-Kishner reductions of the keto acid VIII failed to yield 6,8-di-(methylthio)-octanoic acid (X). Wolff-Kishner reduction in diethylene glycol⁸ at 200° gave low yields (ca. 25%) of products showing little or no infrared carbonyl absorption. Although the carbonyl was apparently reduced, elemental analysis showed the loss of one sulfur per molecule. Additional modification of the molecule was shown by ultraviolet absorption maxima at 228 m μ ($E_{1\%}^{1\text{cm}}$ 318) and 255 m μ ($E_{1\%}^{1\text{cm}}$ 140) and by low neutralization equivalents.

In a modification of the above method, the hydrazone of the hydrazine salt of the keto acid VIII was prepared by reaction with hydrazine hydrate. This product, isolated as an oil, was found to contain 17.1% nitrogen (calcd. 18.8%). The infrared absorption spectrum was characterized by the presence of the carboxylate group and the absence of carbonyl absorption. The hydrazone hydrazine salt was heated at 160° for six hours with sodium ethoxide. This product also showed loss of sulfur (ca. 50%), absence of the carbonyl group and ultraviolet absorption maxima at 227 m μ ($E_{1\%}^{1\text{cm}}$ 748) and 260 m μ ($E_{1\%}^{1\text{cm}}$ 69). The infrared absorption spectrum did not show the presence of α,β -unsaturation.

Clemmensen reductions also gave little or no carbonyl reduction. Under most conditions used, sulfur was eliminated.

A refluxing ethanol-hydrochloric acid-zinc system gave a mixture of an acidic and a neutral product. The morpholine salt of the acidic fraction showed strong carbonyl and carboxylate infrared absorption. None of the reduced acid X was isolated.

A crystalline acid (m.p. 52–54°) was obtained from a refluxing 6 *N* hydrochloric acid-zinc system.

(8) Huang-Minlon, *THIS JOURNAL*, **68**, 2487 (1946).

The infrared spectrum of the sodium salt showed strong carbonyl and carboxylate absorption, and elemental analysis indicated the loss of one sulfur per molecule. Both terminal unsaturation and α,β -unsaturation were eliminated on the basis of infrared and ultraviolet spectra. Similar reactions at room temperature also eliminated sulfur. Refluxing glacial acetic acid-zinc systems gave rise to the crystalline acid (m.p. 52–54°) described above.

Only starting material was isolated from low temperature reactions in ether-6 *N* hydrochloric acid-zinc systems.

Reduction of the keto acid VIII to DL-6,8-di-(methylthio)-octanoic acid was accomplished in two steps. First the carbonyl group was reduced to a hydroxyl with sodium borohydride in aqueous methanol. The reduction mixture on acidification and extraction yielded an oil. Distillation of this oil yielded the δ -lactone IX. The second stage of reduction was accomplished by heating the δ -lactone IX with phosphorus and iodine in glacial acetic acid. In this reaction the amount of iodine used was critical. Best results were obtained using a 1:10 weight ratio of iodine to lactone. Lesser amounts of iodine resulted in incomplete reduction; larger amounts yielded iodine-containing products. Isolation of pure DL-6,8-di-(methylthio)-octanoic acid (X) from such impure products was unsuccessful. Under optimum conditions the acid was isolated as an oil which was partially purified by distillation. This acid was purified and characterized as the *l*-ephedrine salt.

DL-6,8-Di-(methylthio)-octanoic acid showed no activity in the enzymatic POF assay.⁹

The conversion of the acid X to DL- α -lipoic acid (XI) was studied extensively. Considerable attention was paid to acid hydrolytic reactions since methionine was converted to homocystine by this method.⁹ Demethylation was studied using the following reagents: 50% aqueous sulfuric acid (85°), 1:1 glacial acetic acid-66% sulfuric acid (85°), 85% phosphoric acid (85°), hydrobromic acid in glacial acetic acid (85°), hydrogen bromide (80–130°), 2:1 55% hydriodic acid-glacial acetic acid (85°), thiuronium bromide (110–160°), thiuronium chloride (110–160°), pyridinium chloride (110–150°), thiourea and iron (160°), thiourea and zinc (160°), boron trifluoride and glacial acetic acid (110°), boron trifluoride and thioacetic acid (100°), and *p*-thiocresol.

The products from these reactions were not separated or characterized. Dr. George E. Boxer of

(9) L. W. Buntz and V. du Vigneaud, *J. Biol. Chem.*, **99**, 139 (1932).

these laboratories examined the products of these reactions for POF activity.³ The activities observed indicated that low yields of α -lipoic acid had been formed in these reactions.

Acknowledgment.—We are indebted to Dr. N. R. Trenner, Messrs. R. W. Walker, F. W. Bacher and colleagues for the infrared and ultraviolet absorption spectra, to Mr. R. N. Boos and his associates for the elemental analyses and to Dr. J. B. Conn and his associates for the molecular weights reported herein.

Experimental

α -Methylthio- γ -butyrolactone.—A solution of 37.7 g. of α -bromo- γ -butyrolactone in 50 ml. of methanol was cooled while 20.3 g. of sodium methyl mercaptide dissolved in 225 ml. of methanol was added slowly. After standing at room temperature for one hour the reaction mixture was concentrated *in vacuo* and the residual product was diluted with 100 ml. of water. The product was isolated by extraction with three 50-ml. portions of chloroform and the combined extracts were washed with water and dried over anhydrous magnesium sulfate. The anhydrous extract was filtered and concentrated *in vacuo* to yield 19.7 g. (51%) of residual oil.

The product now was distilled through a short Vigreux column and a fraction was collected boiling at 64.0–66.5° (0.1 mm.), weight 11.2 g. (29%), n_D^{25} 1.5040, $\lambda_{\max}^{CS_2}$ 5.68 μ .

Anal. Calcd. for $C_6H_8O_2S$ (132.18): C, 45.43; H, 6.10; S, 24.26. Found: C, 45.65; H, 5.80; S, 24.50; mol. wt. (ebullioscopic), 157 \pm 5.

2,4-Di-(methylthio)-butyric Acid (III).—A solution of 10.8 g. of α -methylthio- γ -butyrolactone in 20 ml. of toluene was added to a stirred suspension of 7 g. of sodium methyl mercaptide in 30 ml. of toluene. The mixture was stirred for one hour at room temperature. After standing overnight the toluene was distilled off *in vacuo*. The residue was fused at 165–170° for 30 minutes; when the fused product had cooled to 100° it was dissolved in 120 ml. of water. The aqueous solution was acidified to pH 3 with concentrated hydrochloric acid and extracted with chloroform. The acidic fraction was isolated by extraction with saturated aqueous sodium bicarbonate followed by acidification to pH 3 with concentrated hydrochloric acid and chloroform extraction. The chloroform solution of the acidic product was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to yield 6.9 g. (48%) of product.

The product was distilled *in vacuo* in a von Braun flask and the product was collected at 154–158° (0.15 mm.), bath temperature 184°, weight 2.9 g. (20%), n_D^{25} 1.5267, neut. equiv. 184 (calcd. 180), $\lambda_{\max}^{CS_2}$ 5.85 μ .

Anal. Calcd. for $C_6H_{12}O_2S_2$ (180.28): C, 39.97; H, 6.71; S, 35.57. Found: C, 40.60; H, 6.54; S, 33.22; mol. wt. (ebullioscopic), 181 \pm 5.

2,4-Dibromobutyric Acid (II).—The method of Plieninger⁴ was modified as follows: Four ml. of phosphorus tribromide was added to 198 g. of γ -butyrolactone and the reaction mixture was heated to 100°. The mixture was stirred while 328 g. of bromine was added dropwise (3 hours) beneath the surface of the liquid. The temperature was maintained at 110–115°; during the first hour temperature was maintained by the rate of bromine addition. When the rate of bromine uptake decreased (ca. 1.5–2 hours), 1 ml. of phosphorus tribromide was added and heat was applied to maintain reaction temperature. The addition of bromine was continued until hydrogen bromide evolution was evident. At that stage the addition of bromine was discontinued and the product was stirred and cooled to room temperature. The product was sufficiently pure for subsequent reactions.

2,4-Di-(methylthio)-butyric Acid (III).—One hundred grams of methyl mercaptan was added to a cold stirred solution of 78 g. of sodium methoxide in 750 ml. of methanol. In the course of 15 minutes 105 g. of 2,4-dibromobutyric acid was added to the cold stirred mercaptide solution. When the addition was complete the mixture was refluxed for one hour and concentrated *in vacuo* on the water-bath. The residue was diluted with 500 ml. of water and acidified

to pH 3 with concentrated hydrochloric acid. The product was isolated by chloroform extraction and the acidic fraction was separated by bicarbonate extraction followed by acidification to pH 3 with concentrated hydrochloric acid and chloroform extraction. The chloroform solution of the acidic product was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to yield 31.7 g. (43%) of 2,4-di-(methylthio)-butyric acid, n_D^{25} 1.5276, neut. equiv. 183 (calcd. 180).

The product was identical with an analytical sample of 2,4-di-(methylthio)-butyric acid prepared from α -methylthio- γ -butyrolactone. Reaction with diazomethane yielded methyl 2,4-di-(methylthio)-butyrate. The yield was 64% after distillation.

Methyl 2,4-Di-(methylthio)-butyrate.—A solution of 1.32 g. of 2,4-di-(methylthio)-butyric acid in 20 ml. of anhydrous ether was cooled and an ethereal solution of diazomethane (10% excess) was added. The reaction was worked up in the usual manner and the solution was concentrated *in vacuo* to yield 1.37 g. of oil. The ester was distilled in a von Braun flask. A fraction was collected boiling at 72–74° (0.17 mm.), bath temperature 80–90°, weight 0.6 g. (40%), n_D^{25} 1.5097, $\lambda_{\max}^{CH_3OH}$ 246 μ (ϵ 610).

Anal. Calcd. for $C_7H_{14}O_2S_2$ (194.30): C, 43.27; H, 7.25; S, 33.00. Found: C, 43.97; H, 6.86; S, 32.79; mol. wt. (ebullioscopic), 226 \pm 10.

2,4-Di-(methylthio)-butyryl Chloride (IV).—2,4-Di-(methylthio)-butyric acid (0.1 mole) was stirred and cooled in an ice-bath while 14 g. of thionyl chloride was added dropwise in the course of 15 minutes. The reaction mixture was stirred for one hour and the excess thionyl chloride and volatile by-products were removed *in vacuo*.¹⁰ The product was distilled *in vacuo* in a von Braun flask (bath temperature 120–130°) to yield 9.2 g. (50%) of 2,4-di-(methylthio)-butyryl chloride, b.p. 93–94° (2–3 mm.), n_D^{25} 1.5340.

The product was identified by conversion to methyl 2,4-di-(methylthio)-butyrate. Treatment with 50 ml. of methanol, concentration *in vacuo* and distillation yielded methyl 2,4-di-(methylthio)-butyrate, b.p. 66.0–68.0° (0.12 mm.), weight 6.94 g. (70%), n_D^{25} 1.5094.

Ethyl [2,4-Di-(methylthio)-butyryl]-acetate (VI).—Magnesium ethoxide (50 g.) was suspended in 440 ml. of anhydrous ether and 81.3 g. of ethyl *t*-butylmalonate was added dropwise to the stirred suspension in the course of 15 minutes. When the exothermic reaction was complete, the reaction mixture was refluxed for 15 minutes. The reaction mixture was cooled and 0.8 mole of 2,4-di-(methylthio)-butyryl chloride¹¹ was added at a rate sufficient to induce gentle refluxing. When addition was complete, the mixture was refluxed for one hour. The mixture was cooled and acidified with 2 *N* sulfuric acid. The ether phase was separated. The aqueous phase was extracted twice with ether and the combined ether extracts were washed with water and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated *in vacuo*. The residue was dissolved in anhydrous benzene and final traces of water were removed by azeotropic distillation. When the anhydrous benzene solution had cooled to room temperature, 4 g. of anhydrous *p*-toluenesulfonic acid was added and the solution was refluxed for three hours. Carbon dioxide and ethylene were detected in the gas generated during reflux. When gas evolution had virtually ceased, the solution was cooled and washed with saturated aqueous sodium bicarbonate. The benzene phase was washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The residue (150 g.) was distilled *in vacuo* through a short Vigreux column to remove the low boiling fractions (<95° (0.03 mm.)). The higher boiling fractions were obtained by distillation in a von Braun flask.

Fraction 1: b.p. 108–116° (0.08 mm.), bath temperature 167°, weight 16.9 g. (8%), n_D^{25} 1.5025.

Fraction 2: b.p. 116–121° (0.08 mm.), bath temperature 167–172°, weight 31.0 g. (29%), n_D^{25} 1.5088, $\lambda_{\max}^{CH_3OH}$ 246 μ (ϵ 1237), $\lambda_{\max}^{CH_3OH}$ 294 μ (ϵ 481), $\lambda_{\max}^{CHCl_3}$ 5.77 and 5.85 μ .

(10) Later experiments showed that the product could be purified more conveniently when the reaction was carried out in anhydrous benzene solution.

(11) Crude residual product. Later results showed that the acid chloride distilled readily and the use of the purified reactant greatly improved the yield and ease of isolation of the condensation product.

Anal. Calcd. for $C_{10}H_{18}O_3S_2$ (250.86): C, 47.98; H, 7.24; S, 25.62. Found: C, 48.25; H, 7.15; S, 25.75; mol. wt. (ebullioscopic), 255 ± 3 .

Methyl 4-Carboxy-4-[2,4-di-(methylthio)-butyryl]-butyrate (VII).—Twenty grams of ethyl [2,4-di-(methylthio)-butyryl]-acetate and 5 g. of 30% methanolic Triton B were stirred while 7 g. of methyl acrylate was added during a 15-minute period. The temperature rose from 25 to 35° during the addition and ultimately reached 50°. The mixture was cooled. After the initial exothermic reaction subsided, the mixture was stirred at 50–55° for 48 hours. The reaction mixture was cooled and 100 ml. of chloroform and 50 ml. of 1 N hydrochloric acid were added. The chloroform phase was separated, washed with water and dried over anhydrous magnesium sulfate. The chloroform solution was filtered and concentrated *in vacuo* to yield 25 g. of oil. The product was distilled *in vacuo* in a von Braun flask and a fraction was collected boiling at 137–186° (5 μ), bath temperature 200–235°, weight 15 g. (55%), n_D^{25} 1.5039, n_D^{20} 1.4989, n_D^{15} 1.4939, n_D^{10} 1.4889, n_D^5 1.4839, n_D^0 1.4789, n_D^{-5} 1.4739, n_D^{-10} 1.4689, n_D^{-15} 1.4639, n_D^{-20} 1.4589, n_D^{-25} 1.4539, n_D^{-30} 1.4489, n_D^{-35} 1.4439, n_D^{-40} 1.4389, n_D^{-45} 1.4339, n_D^{-50} 1.4289, n_D^{-55} 1.4239, n_D^{-60} 1.4189, n_D^{-65} 1.4139, n_D^{-70} 1.4089, n_D^{-75} 1.4039, n_D^{-80} 1.3989, n_D^{-85} 1.3939, n_D^{-90} 1.3889, n_D^{-95} 1.3839, n_D^{-100} 1.3789, n_D^{-105} 1.3739, n_D^{-110} 1.3689, n_D^{-115} 1.3639, n_D^{-120} 1.3589, n_D^{-125} 1.3539, n_D^{-130} 1.3489, n_D^{-135} 1.3439, n_D^{-140} 1.3389, n_D^{-145} 1.3339, n_D^{-150} 1.3289, n_D^{-155} 1.3239, n_D^{-160} 1.3189, n_D^{-165} 1.3139, n_D^{-170} 1.3089, n_D^{-175} 1.3039, n_D^{-180} 1.2989, n_D^{-185} 1.2939, n_D^{-190} 1.2889, n_D^{-195} 1.2839, n_D^{-200} 1.2789, n_D^{-205} 1.2739, n_D^{-210} 1.2689, n_D^{-215} 1.2639, n_D^{-220} 1.2589, n_D^{-225} 1.2539, n_D^{-230} 1.2489, n_D^{-235} 1.2439, n_D^{-240} 1.2389, n_D^{-245} 1.2339, n_D^{-250} 1.2289, n_D^{-255} 1.2239, n_D^{-260} 1.2189, n_D^{-265} 1.2139, n_D^{-270} 1.2089, n_D^{-275} 1.2039, n_D^{-280} 1.1989, n_D^{-285} 1.1939, n_D^{-290} 1.1889, n_D^{-295} 1.1839, n_D^{-300} 1.1789, n_D^{-305} 1.1739, n_D^{-310} 1.1689, n_D^{-315} 1.1639, n_D^{-320} 1.1589, n_D^{-325} 1.1539, n_D^{-330} 1.1489, n_D^{-335} 1.1439, n_D^{-340} 1.1389, n_D^{-345} 1.1339, n_D^{-350} 1.1289, n_D^{-355} 1.1239, n_D^{-360} 1.1189, n_D^{-365} 1.1139, n_D^{-370} 1.1089, n_D^{-375} 1.1039, n_D^{-380} 1.0989, n_D^{-385} 1.0939, n_D^{-390} 1.0889, n_D^{-395} 1.0839, n_D^{-400} 1.0789, n_D^{-405} 1.0739, n_D^{-410} 1.0689, n_D^{-415} 1.0639, n_D^{-420} 1.0589, n_D^{-425} 1.0539, n_D^{-430} 1.0489, n_D^{-435} 1.0439, n_D^{-440} 1.0389, n_D^{-445} 1.0339, n_D^{-450} 1.0289, n_D^{-455} 1.0239, n_D^{-460} 1.0189, n_D^{-465} 1.0139, n_D^{-470} 1.0089, n_D^{-475} 1.0039, n_D^{-480} 0.9989, n_D^{-485} 0.9939, n_D^{-490} 0.9889, n_D^{-495} 0.9839, n_D^{-500} 0.9789, n_D^{-505} 0.9739, n_D^{-510} 0.9689, n_D^{-515} 0.9639, n_D^{-520} 0.9589, n_D^{-525} 0.9539, n_D^{-530} 0.9489, n_D^{-535} 0.9439, n_D^{-540} 0.9389, n_D^{-545} 0.9339, n_D^{-550} 0.9289, n_D^{-555} 0.9239, n_D^{-560} 0.9189, n_D^{-565} 0.9139, n_D^{-570} 0.9089, n_D^{-575} 0.9039, n_D^{-580} 0.8989, n_D^{-585} 0.8939, n_D^{-590} 0.8889, n_D^{-595} 0.8839, n_D^{-600} 0.8789, n_D^{-605} 0.8739, n_D^{-610} 0.8689, n_D^{-615} 0.8639, n_D^{-620} 0.8589, n_D^{-625} 0.8539, n_D^{-630} 0.8489, n_D^{-635} 0.8439, n_D^{-640} 0.8389, n_D^{-645} 0.8339, n_D^{-650} 0.8289, n_D^{-655} 0.8239, n_D^{-660} 0.8189, n_D^{-665} 0.8139, n_D^{-670} 0.8089, n_D^{-675} 0.8039, n_D^{-680} 0.7989, n_D^{-685} 0.7939, n_D^{-690} 0.7889, n_D^{-695} 0.7839, n_D^{-700} 0.7789, n_D^{-705} 0.7739, n_D^{-710} 0.7689, n_D^{-715} 0.7639, n_D^{-720} 0.7589, n_D^{-725} 0.7539, n_D^{-730} 0.7489, n_D^{-735} 0.7439, n_D^{-740} 0.7389, n_D^{-745} 0.7339, n_D^{-750} 0.7289, n_D^{-755} 0.7239, n_D^{-760} 0.7189, n_D^{-765} 0.7139, 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