Optical Resolution of *N*-Acyl-DL-amino Acids by Preferential Crystallization Procedure. Preparation of L-DOPA and L-α-Methyl DOPA[1]

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To develop the practical method for the production of L-DOPA and L-α-methyl DOPA, the optical resolution of their precursors, *N*-acetyl-DL-3-(3,4-methylenedioxyphenyl)alanine and *N*-acetyl-DL-3-(3,4-methylenedioxyphenyl)-2-methylalanine, was studied. The di-*n*-butylamine salt of *N*-acetyl-DL-3-(3,4-methylenedioxyphenyl)alanine and the hydrazine salt of *N*-acetyl-DL-3-(3,4-methylenedioxyphenyl)-2-methylalanine were resolved by preferential crystallization procedures, and optically pure isomers of both amino acids were obtained in good yield. The present simple resolution method using amine salts is expected to be applied more generally for resolution of *N*-acyl-DL-amino acids.

L-3-(3,4-Dihydroxyphenyl)alanine (L-DOPA) and L-3-(3,4-dihydroxyphenyl)-2-methylalanine (L-α-methyl DOPA) are important substances in biochemical and pharmaceutical fields,[2,3] and their markets have been expanding rapidly in recent years. It is therefore desirable to establish practical methods for the production of optically active DOPA and α-methyl DOPA.

Generally, optical resolution of the synthesized DL amino acids is more facile and practical for the production of optically active amino acids than the asymmetric synthesis of amino acids, because the latter method has not yet reached the stage of practicability and is still in a state of investigation. Among the various techniques for optical resolution of DL amino acids,[4] the preferential crystallization procedure[5] is considered to be one of the most useful for industrial application since it enables the desired optically active isomer to crystallize preferentially from a supersaturated solution of DL amino acid. However, it has the disadvantage that it cannot be applied to all kinds of amino acids because most amino acids form racemic compounds and are not suitable for this resolution method. In order to resolve this problem, a method of resolution using aromatic sulfonic acid has recently been developed by us and reported in the previous papers.[6-9] In this manner optical resolution of DL-DOPA and DL-3-(3,4-methylenedioxyphenyl)-2-methylalanine (DL-MDPMA), α-methyl DOPA precursor, became possible as the salts with 2-naphthol-6-sulfonic acid and *p*-phenolsulfonic acid, respectively.[9]

On the other hand, the synthetic route via acyl derivatives has often been used for the synthesis of DL amino acids. For example, DL–DOPA is synthesized in good yield via *N*-acetyl-DL-3-(3,4-methylenedioxyphenyl)alanine (*N*-Ac-DL-MDPA) from piperonal and acetylglycine.[10] In such cases, it is more desirable that an intermediate in the process of amino acid synthesis be easily resolved into the optical antipodes, and the undesired antipode be easily racemized to the DL form and then reused for the resolution step. In this study, therefore, the optical resolution of *N*-Ac-DL-MDPA and *N*-acetyl-DL-3-(3,4-methylenedioxyphenyl)-2-methylalanine (*N*-Ac-DL-MDPMA) have been investigated as a first approach to establish the general method for the optical resolution of *N*-acyl-DL-amino acids by preferential crystallization procedure.

Until now, the ammonium salts of the acyl derivatives of certain amino acids, including DL-tryptophan,[11] DL-phenylalanine,[12] DL-valine,[12] DL-methionine,[12] DL-serine,[13] DL-phenylglycine,[14] and DL-MDPA,[15] have been resolved by the preferential crystallization procedure. Although this type of resolution using the ammonium salts is very valuable, its application is restricted to a limited number of amino acids. In fact, the ammonium salt of *N*-Ac-DL-MDPMA could not be resolved since it formed a racemic compound. With respect to the ammonium salt of *N*-Ac-DL-MDPA, it formed a racemic mixture and was resolvable. However, the operation was not so easy in practice and the resolution results was unsatisfactory since the form of the crystals was unsuitable for the filtration process after crystallization.[1] Generally speaking, even though the ammonium salts of acyl derivatives are resolvable, the practical resolution is often difficult in cases where the salts have no adequate solubility and no suitable characteristics for easy handling.

Therefore, we attempted the optical resolution of the acylamino acids in the form of their salts with commercially available (optically inactive) amines instead of the ammonium salts. This idea is similar to that in our previous method using aromatic sulfonates. Namely, amines vary greatly in their properties and readily form salts with all kinds of *N*-acylamino acids, so that it becomes very easy to screen the salts suitable for the preferential crystallization procedure. Thus, we prepared a wide variety of amine salts of *N*-Ac-DL-MDPA and of *N*-Ac-DL-MDPMA, and screened the salts forming racemic mixtures by comparing the infrared spectrum, melting point, and solubility relationships of the racemic modifications and the optically active isomers.[8] As a result, it was found that the di-*n*-butylamine salt of *N*-Ac-DL-MDPA (*N*-Ac-DL-MDPA·DBA) and the hydrazine salt of *N*-Ac-DL-MDPMA (*N*-Ac-DL-MDPMA·HZ) readily crystallize as a racemic mixture from water, and the crystals have adequate solubility and suitable characteristics for easy handling. Then both salts were resolved by the usual manner described in our previous reports[8,9] and in the Experimental Section (see Tables I and II).

The optically active *N*-Ac-MDPA·DBA and *N*-Ac-MDPMA·HZ obtained above had an optical purity of about 98% on the average. When the optical purity is not satisfactory and further purification is required, the optically impure crystals can be purified without loss of the optically active isomer using the property of a saturated solution of the racemic mixture that it no longer dissolved the optically active isomer. Thus obtained optically active *N*-Ac-MDPA·DBA and *N*-Ac-MDPMA·HZ were decomposed with HCl to yield optically active *N*-Ac-MDPA and *N*-Ac-MDPMA quantitatively. The undesired *N*-Ac-D-MDPA was completely racemized by melting and the resulting *N*-Ac-DL-MDPA was reused for the resolution. However, *N*-Ac-D-MDPMA cannot be racemized in the usual way used for *N*-acylamino acids, because of the character of substitution at the optically active α position. The optically active *N*-Ac derivatives were converted to L-DOPA and L-α-methyl DOPA by the usual hydrolysis.

Table I
Successive Resoluions of *N*-Ac-DL-MDPA·DBA[a]

Expt	Amount of addition: DL form, g	Amount of addition: Active form, g	Composition of solution: DL form, g	Composition of solution: Active form, g	Separated crystals: Yield, g	Separated crystals: Optical purity,[b] %
1 (L)	37.50	4.00	37.50	4.00	8.95	97.8
2 (D)	9.23		36.85[c]	4.65[c]	7.93	97.7
3 (L)	8.18		38.50[c]	3.00[c]	8.36	97.5
4 (D)	8.62		36.45[c]	5.05[c]	7.81	98.2
5 (L)	8.05		38.98[c]	2.52[c]	8.27	97.5
6 (D)	8.53		36.06[c]	5.44[c]	8.12	97.6
Mean	8.52		37.39[c]	4.11[c]	8.24	97.7

[a] Resolutions were carried out at 35° on a 50-ml scale. Crystallization time was 90 min in every case. [b] The optical purity was calculated with the assumption that the specific rotation of the pure sample is $[\alpha]^{25}D \pm 42.4°$ (*c* 2, water). [c] Values calculated theoretically from analysis of separated crystals.

Table II
Successive Resolutions of DL-*N*-Ac-MDPMA·HZ[a]

Expt	Amount of addition: DL form, g	Amount of addition: Active form, g	Composition of solution: DL form, g	Composition of solution: Active form, g	Separated crystals: Yield, g	Separated crystals: Optical purity,[b] %
1 (L)	16.50	2.00	16.50	2.00	3.96	100
2 (D)	4.00		16.59[c]	1.91[c]	4.03	97.5
3 (L)	4.08		16.53[c]	1.97[c]	4.11	96.8
4 (D)	4.24		16.54[c]	1.96[c]	4.05	98.2
Mean	4.11		16.54[c]	1.96[c]	4.04	98.1

[a] Resolutions were carried out at 25° on a 50-ml scale. Crystallization time was 60 min in every case. [b] The optical purity was calculated with the assumption that the specific rotation of the pure sample is $[\alpha]^{25}D \pm 87.8°$ (*c* 0.5, MeOH). [c] Values calculated theoretically from analysis of separated crystals.

The optical resolution methods now presented are very advantageous providing the optical isomers are available because they require neither an optically active resolving agent nor conversion of the intermediates into complicated derivatives, the yield per unit volume is very high, and the operation is so simple that all processes are expected to be operated automatically in a sequence control system. Therefore, application of the present method for the industrial production of L-DOPA and L-α-methyl DOPA is considered to be very promising if combined with a proper synthetic method for *N*-Ac-DL-MDPA and *N*-Ac-DL-MDPMA.

Furthermore, although we cannot find a guiding rule that predicts the kind of amine salts which can be resolved by the preferential crystallization procedure, it becomes very easy to screen the suitable salts by the use of various amines. Therefore, the present simple resolution method using amine salts is expected to be applied more generally for resolution of synthetic acylamino acids.

Experimental Section

Materials. *N*-Ac-DL-MDPA was prepared in our laboratory from piperonal and *N*-acetylglycine via the azlactone as usual,[10,16] colorless needles, mp 180–182° (lit.[16] mp 178–180°). Anal. Calcd for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; N, 5.58. Found: C, 57.22; H, 5.32; N, 5.67. A small amount of *N*-Ac-D-MDPA used for initial seed crystals was obtained by the optical resolution of *N*-Ac-DL-MDPA by asymmetric hydrolysis using a mold aminoacylase preparation.[16] The optically active *N*-Ac-L- and -D-MDPA used for seed crystals were obtained by the present preferential crystallization procedure. *N*-Ac-L-MDPA: colorless needles, $[\alpha]^{20}D$ +53.9° (*c* 1.5, EtOH), mp 158–159° [lit.[16] $[\alpha]^{13}D$ +53.4° (*c* 2.262, EtOH), mp 158–159°]. *N*-Ac-D-MDPA: colorless needles, $[\alpha]^{20}D$ −53.9° (*c* 1.5, EtOH), mp 158–159° [lit.[16] $[\alpha]^{18}D$ −53.4° (*c* 1.841, EtOH), mp 158–159°].

N-Ac-L-, -D-, and -DL-MDPMA were obtained as usual[17] by acetylating L-, D-, and DL-MDPMA, which were used in the previous report.[9] *N*-Ac-L-MDPMA: colorless needles, $[\alpha]^{20}D$ −58.8° (*c* 0.5, MeOH), mp 219–220° [lit.[17] $[\alpha]^{20}D$ −58.0° (*c* 0.5, MeOH), mp 214–215°]. *N*-Ac-D-MDPMA: colorless needles, $[\alpha]^{20}D$ +58.8° (*c* 0.5, MeOH), mp 219–220° [lit.[17] $[\alpha]^{20}D$ +58.0° (*c* 0.5, MeOH), mp 214–215°]. *N*-Ac-DL-MDPMA: colorless needles, mp 191–192° (lit.[17] mp 189–191°). Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28. Found: C, 58.78; H, 5.65; N, 5.30. Di-*n*-butylamine and hydrazine hydrate were obtained from Katayama Chemical Industries Co., Ltd.

Analyses. All samples were dried overnight at 45–50° unless otherwise noted. Melting points were measured with a Yamato MP-21 melting point apparatus in an unsealed capillary tube and are uncorrected. Infrared spectra of samples were determined in KBr disks using a Shimadzu infrared spectrophotometer, Model IR-27G. Optical rotations were measured with a Perkin-Elmer 141 automatic polarimeter. Elemental analyses were performed with a Perkin-Elmer 240 elemental analyzer. Solubility was determined by approaching saturation equilibrium from both undersaturation and supersaturation. Solute concentration was measured with a Karl Zeiss immersion refractometer.

Preparation of *N*-Ac-L-, -D-, and -DL-MDPA·DBA. Di-*n*-butylamine (133.0 g, 1.03 mol) and water (350 ml) were added to *N*-Ac-DL-MDPA (251.2 g, 1 mol). The mixture was heated, treated with charcoal, and filtered. The filtrate was allowed to stand in a refrigerator overnight. The precipitate was collected, washed with cold water, and dried in vacuo to give *N*-Ac-DL-MDPA·DBA (267.4 g), mp 142–145°. A second crop was obtained by successive concentrations of the combined filtrates. The total yield was 355.2 g (93.4%). The products were almost pure and could be used for optical resolution without further purification. Recrystallization from water gave colorless prisms, mp 143–145°. Anal. Calcd for $C_{20}H_{32}N_2O_5$: C, 63.14; H, 8.48; N, 7.36. Found: C, 62.83; H, 8.50; N, 7.18. Solubility in water (g/100 ml): 22.8 (15°), 26.5 (25°), 38.3 (35°).

The optically active *N*-Ac-L- and -D-MDPA·DBA were prepared from *N*-Ac-L- and -D-MDPA, respectively, in the same way as described above. The L isomer: $[\alpha]^{25}D$ +42.4° (*c* 2, H_2O); mp 160–162°. Anal. Found: C, 62.96; H, 8.68; N, 7.14. Solubility in water (g/100 ml): 12.7 (15°), 13.3 (25°), 16.6 (35°). The D isomer: $[\alpha]^{25}D$ −42.4° (*c* 2, water); mp 160–162°. The infrared spectra of *N*-Ac-L-, -D-, and -DL-MDPA·DBA in KBr were identical: ir (KBr) 3225, 3050, 2950, 2870, 2500–2100, 1625, 1590–1550, 1500, 1445, 1380, 1300, 1240, 1193, 1035, 930, 855, 823, 812, 735 cm^{-1}.

Optical Resolution of *N*-Ac-DL-MDPA·DBA. In a typical experiment, *N*-Ac-DL-MDPA·DBA (37.50 g) and *N*-Ac-L-MDPA·DBA (4.00 g) were dissolved in water (50 ml) at elevated temperature. The solution was cooled to 35°, seeded with fine pulverized crystals of *N*-Ac-L-MDPA·DBA (0.10 g), and stirred for 90 min at the same temperature. The precipitated crystals were collected by filtration, washed with a small amount of cold water (2 ml), and dried to give *N*-Ac-L-MDPA·DBA (8.95 g). Its optical purity was 97.8%, $[\alpha]^{25}D$ +41.4° (*c* 2, H_2O).

After the separation of the L isomer, *N*-Ac-DL-MDPA·DBA (9.23 g) and a small amount of water were added to the mother liquor in order to prepare the supersaturated solution of almost the same composition as in the previous resolution except that the predominant isomer was D isomer. The amounts of the addition were adjusted by refractometric measurement and weighing according to a standard curve previously constructed. The solution thus obtained was cooled to 35°, seeded with *N*-Ac-D-MDPA·DBA (0.10 g), and stirred. After 90 min, the precipitated crystals were treated in the same manner as described above to yield *N*-Ac-D-MDPA·DBA (7.93 g), which had 97.7% optical purity. By repeating these procedures, L and D isomers were successively obtained. The examples of the several runs are shown in Table I.

Purification of Optically Impure *N*-Ac-MDPA·DBA. The optical isomers separated by the above procedure are practically pure. When further purification is necessary, it can easily be performed by ordinary recrystallization. On the other hand, optically impure *N*-Ac-L-MDPA·DBA could be purified without loss of op-

tically active isomer as follows. Optically impure *N*-Ac-L-MDPA·DBA (8.53 g, optical purity 85.0%) was dissolved at elevated temperature in a solution comprised of water (3.3 ml) and a saturated solution of *N*-Ac-DL-MDPA·DBA (appropriate amount 10 ml). The mixture was then stirred for 1 hr at 35°. The resulting crystals were collected by filtration, washed with a small amount of water, and dried to give *N*-Ac-L-MDPA·DBA (7.29 g), $[\alpha]^{25}D$ +42.0° (*c* 2, H_2O), optical purity 99.1%. Recrystallization from water gave optically pure *N*-Ac-L-MDPA·DBA, $[\alpha]^{25}D$ +42.4° (*c* 2, H_2O), mp 160–162°.

Optically Active *N*-Ac-L- and -D-MDPA from the Corresponding Di-*n*-butylamine Salts. Optically pure *N*-Ac-L-MDPA·DBA (10.00 g) was dissolved in hot water (25 ml) and decomposed with a slight excess of 5 *N* HCl to liberate the *N*-Ac-L-MDPA. The mixture was allowed to stand in a refrigerator overnight. The precipitate was filtered off, washed with water, and dried to give *N*-Ac-L-MDPA (6.28 g, 95.1%), $[\alpha]^{20}D$ +53.9° (*c* 1.5, EtOH), mp 158–159° [lit.[16] $[\alpha]^{13}D$ +53.4° (*c* 2.262, EtOH), mp 158–159°].

N-Ac-D-MDPA was obtained similarly from *N*-Ac-D-MDPA·DBA and had $[\alpha]^{20}D$ −53.9° (*c* 1.5, EtOH), mp 158–159° [lit.[16] $[\alpha]^{18}D$ −53.4° (*c* 1.841, EtOH), mp 158–159°]. Their specific optical rotations and melting points did not change after recrystallization from water. From the filtrate, di-*n*-butylamine satisfactory for reuse was recovered in 90% yield.

Racemization of *N*-Ac-D-MDPA and Preparation of *N*-Ac-DL-MDPA·DBA. *N*-Ac-D-MDPA (1.00 g) was melted in an unsealed tube by heating at 160–165°. After 15 min, to the solidified crystals, an equivalent amounts of di-*n*-butylamine (0.53 g) and water (5 ml) were added. The mixture was dissolved at elevated temperature, treated with charcoal, and concentrated nearly to dryness. The residual crystals were suspended in acetone, filtered, and dried in vacuo to give *N*-Ac-DL-MDPA·DBA (1.38 g), mp 138–142°. The product could be reused for the resolution step. Recrystallization from water gave pure *N*-Ac-DL-MDPA·DBA as colorless prisms, $[\alpha]^{25}D$ 0.0° (*c* 2, H_2O), mp 142–145°. This sample was found to be identical by admixture and ir comparison with the authentic sample prepared from the starting material.

Preparation of L-DOPA. *N*-Ac-L-MDPA (2.00 g) obtained above was added to a mixture of 20% HCl (40 ml) and phenol (2.0 g). The mixture was refluxed for 17 hr under stirring. After filtration, the filtrate was treated with charcoal and concentrated to dryness to remove excess HCl. The residue was taken up in water (10 ml) and the solution was treated with charcoal, adjusted to pH 5 with 5 *N* NH_4OH containing a small amount of sodium bisulfite, and allowed to stand in a refrigerator overnight. The precipitate was filtered and washed with cold water to give crude L-DOPA (1.12 g, 71.4%). Recrystallization from a diluted sulfurous acid solution afforded colorless needles, $[\alpha]^{20}D$ −12.2° (*c* 4, 1 *N* HCl), mp 278–279° dec [lit.[18] $[\alpha]^{20}D$ −12.1° (*c* 4, 1 *N* HCl)]. Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.85; H, 5.59; N, 7.08.

Preparation of *N*-Ac-L-, -D-, and -DL-MDPMA·HZ. *N*-Ac-DL-MDPMA·HZ was obtained from *N*-Ac-DL-MDPMA (265.1 g, 1 mol) and hydrazine hydrate (52.6 g, 1.05 mol) in the same way as *N*-Ac-DL-MDPA·DBA. Total yield was 216.7 g (97.5%). The products were almost pure and could be used for optical resolution without further purification. Recrystallization from water gave colorless needles, mp 189–190° dec. Anal. Calcd for $C_{13}H_{19}N_3O_5$: C, 52.51; H, 6.44; N, 14.13. Found: C, 52.61; H, 6.51; N, 14.01. Solubility in water (g/100 ml): 17.0 (10°), 21.1 (25°), 31.7 (40°).

The optically active forms were prepared in the same way. The L isomer: $[\alpha]^{25}D$ +87.8° (*c* 0.5, MeOH), mp 206–207° dec. Anal. Found: C, 52.59; H, 6.54; N, 14.15. Solubility in water (g/100 ml): 10.6 (10°), 12.8 (25°), 17.3 (40°). The D isomer: $[\alpha]^{25}D$ −87.8° (*c* 0.5, MeOH), mp 206–207° dec. The infrared spectra of *N*-Ac-L-, -D-, and -DL-MDPMA·HZ in KBr were identical: ir (KBr) 3320, 3120, 2120, 1650, 1625, 1565–1490, 1440, 1395, 1365, 1255, 1230, 1190, 1100, 1035, 930, 825, 705, 645 cm^{-1}.

Optical Resolution of *N*-Ac-DL-MDPMA·HZ. *N*-Ac-DL-MDPMA·HZ (16.50 g) and *N*-Ac-L-MDPMA·HZ (2.00 g) were dissolved in water (50 ml) at elevated temperature. The solution was cooled to 25°, seeded with *N*-Ac-L-MDPMA·HZ (0.05 g), and stirred at the same temperature. After 60 min, the precipitated crystals were filtered and washed with cold water (2 ml). *N*-Ac-L-MDPMA·HZ (3.96 g) thus obtained was optically pure, $[\alpha]^{25}D$ +87.8° (*c* 0.5, MeOH).

After the separation of the L isomer, *N*-Ac-DL-MDPMA·HZ (4.00 g) and a small amount of water were added to the mother liquor in the same way as described in the case of *N*-Ac-MDPA·DBA. The solution was cooled to 25°, seeded with *N*-Ac-D-MDPMA·HZ (0.05 g), and stirred for 60 min. The precipitated crystals were treated as described above to yield *N*-Ac-D-MDPMA·HZ (4.03 g), which had 97.5% optical purity, $[\alpha]^{25}D$ −85.6° (*c* 0.5, MeOH). The first several runs on a 50-ml scale are given in Table II.

Purification of Optically Impure *N*-Ac-MDPMA·HZ. *N*-Ac-L-MDPMA·HZ (10.00 g, optical purity 56.5%) was dissolved in water (21 ml) by heating. The solution was then stirred for 3 hr at 25°. The precipitated crystals were collected by filtration to give optically pure *N*-Ac-L-MDPMA·HZ (5.52 g), $[\alpha]^{25}D$ +87.8° (*c* 0.5, MeOH), mp 205–206° dec.

Optically Active *N*-Ac-L- and -D-MDPMA from the Corresponding Hydrazine Salts. The optically pure *N*-Ac-L-MDPMA·HZ (5.00 g) obtained above was dissolved in hot water (50 ml) and decomposed with excess 6 *N* HCl to liberate the *N*-Ac-L-MDPMA. After the mixture was allowed to stand in a refrigerator overnight, the precipitate was filtered, washed with water, and dried in vacuo to yield *N*-Ac-L-MDPMA (4.39, 98.5%), showing $[\alpha]^{25}D$ −58.6° (*c* 0.5, MeOH), mp 218–219°. Recrystallization from MeOH afforded colorless needles, $[\alpha]^{20}D$ −58.8° (*c* 0.5, MeOH), mp 219–220° [lit.[17] $[\alpha]^{20}D$ −58.0° (*c* 0.5, MeOH), mp 214–215°].

N-Ac-D-MDPMA was obtained similarly from *N*-Ac-D-MDPMA·HZ and had $[\alpha]^{20}D$ +58.8° (*c* 0.5, MeOH), mp 219–220° [lit.[17] $[\alpha]^{20}D$ +58.0° (*c* 0.5, MeOH), mp 214–215°].

Preparation of L-α-Methyl DOPA. The *N*-Ac-L-MDPMA (4.00 g) obtained above was hydrolyzed with 20% HCl in the presence of phenol in the same way as described in the preparation of L-DOPA from *N*-Ac-L-MDPA. The total yield of L-α-methyl DOPA·$\frac{3}{2}H_2O$ was 2.57 g (71.5%). Recrystallization from a sulfurous acid solution (0.5%) gave a white powder of L-α-methyl DOPA·$\frac{3}{2}H_2O$, and drying of the sesquihydrate in vacuo at 100° gave the anhydrous form, $[\alpha]^{25}D$ −5.2°, $[\alpha]^{25}_{578}$ −5.5° (*c* 2, 0.1 *N* HCl), mp 306–307° dec [lit.[19] $[\alpha]^{25}D$ −4° (*c* 2, 0.1 *N* HCl) and $[\alpha]^{25}_{578}$ +5.5° (*c* 2, 0.1 *N* HCl) for D-α-methyl DOPA]. Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.75; H, 6.23; N, 6.58.

Registry No.—*N*-Ac-DL-MDPA, 30657-34-2; piperonal, 120-57-0; *N*-acetylglycine, 543-24-8; *N*-Ac-L-MDPA, 28104-71-4; *N*-Ac-D-MDPA, 55629-70-4; *N*-Ac-DL-MDPMA, 23541-10-8; dibutylamine, 111-92-2; *N*-Ac-DL-MDPA·DBA, 55657-00-6; *N*-Ac-L-MDPA·DBA, 55656-80-9; *N*-Ac-D-MDPA·DBA, 55657-01-7; L-DOPA, 59-92-7; *N*-Ac-DL-MDPMA·HZ, 56599-11-2; hydrazine, 302-01-2; *N*-Ac-L-MDPMA·HZ, 56599-12-3; *N*-Ac-D-MDPMA·HZ, 56599-13-4; *N*-Ac-L-MDPMA, 23402-51-9; *N*-Ac-D-MDPMA, 24951-50-6; L-α-methyl DOPA, 555-30-6.

References and Notes

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