3. Solvent removal in vacuo provided a light yellow oil [R_f 0.67; ethyl acetate (5%)/petroleum ether (95%)], which proved to be unstable toward further purification. Formation of silyl enol ether **4** was verified by treatment of the crude material with tetra-*n*-butylammonium fluoride as the trihydrate (631 mg, 2.0 mmol) in THF (2 mL) to provide after purification cyclodecadienone **3** (71% from divinylcyclohexenol **1**).

4: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 6.03 (1 H, d, J = 11.1 Hz), 5.33 (1 H, dt, J = 7.1, 10.3 Hz), 4.87 (1 H, ddd, J = 15.3, 10.3, 4.6 Hz), 4.63 (1 H, dd, J = 15.8, 9.1 Hz), 4.59 (1 H, t, J = 8.5 Hz), 2.35 (1 H, m), 2.08 (2 H, m), 1.98 (1 H, m), 1.44–1.64 (3 H, m), 1.35 (1 H, d, J = 10.3 Hz), 0.92 (6 H, d, J = 6.1 Hz), 0.90 (9 H, s), 0.11 (6 H, s), 0.08 (6 H, s); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 150.18, 132.98, 132.33, 130.33, 127.45, 107.29, 53.80, 32.71, 32.03, 31.70, 28.61, 25.75, 21.30, 20.33, 18.15, -4.31; IR (NaCl, cm^{-1}) 2945, 2846, 1679, 1608, 1466, 1458, 1248, 965, 831, 774; MS (CI), m/e (relative intensity) 309 (6), 308 (23), 307 (M + 1, 89), 291 (36), 279 (24), 249 (15), 175 (100), 119 (26); TLC [ethyl acetate (5%)/petroleum ether (95%)] R_f 0.67.

4-(2-Propyl)-5(*E*)-cyclodecenone (7). Potassium hydride (2.61 mmol) in a mineral oil suspension was washed with pentane (1.0 mL; 3x) and suspended in THF (2.0 mL). The resulting THF suspension could either be employed directly without iodine chemical modification or with iodine pretreatment as described above; yields of the desired rearrangement products **7** and **8** were essentially identical. 18-Crown-6 (690 mg, 2.61 mmol) and divinylcyclohexanol **5** (102 mg, 0.522 mmol) dissolved in a minimum volume of THF (~1.5 mL) were added in a single portion, and the resulting mixture was refluxed for 2 h or stirred at room temperature for 8 h. The reaction was then cooled to -78 °C and quenched with absolute ethanol (1.5 mL) via rapid injection. The resulting slurry was immediately poured into a mixture of petroleum ether (5 mL) and a solution of saturated ammonium chloride (5 mL) and thoroughly shaken. The organic layer was washed with brine (5 mL), dried over sodium sulfate, filtered, and concentrated in vacuo to provide an orange semisolid. Chromatography [silica gel; ether (5%)/petroleum ether (95%)] afforded cyclodecenone **7** (85.5 mg, 85%) as a waxy solid (mp ~28 °C).

7: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 5.30 (1 H, ddd, J = 14.7, 11.0, 3.7 Hz), 4.94 (1 H, dd, J = 14.7, 10.6 Hz), 2.50 (1 H, dd, J = 16.1, 9.9 Hz), 2.12–2.43 (4 H, m), 2.04 (1 H, q, J = 12.6 Hz), 1.93 (2 H, m), 1.77 (2 H, m), 1.63 (2 H, m), 1.48 (1 H, hextet, J = 6.7 Hz), 1.32 (1 H, q, J = 13.4 Hz), 0.86 (3 H, d, J = 6.7 Hz), 0.82 (3 H, d, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 212.52, 137.07, 130.26, 53.16, 45.39, 42.56, 33.07, 31.39, 28.62, 22.15, 20.70, 20.24; IR (NaCl, cm^{-1}) 2913, 2847, 1700, 1428, 1353, 1095, 977; MS (CI), m/e (relative intensity) 195 (M + 1, 33), 177 (100), 121 (47), 95 (12), 81 (7); TLC [ethyl acetate (10%)/petroleum ether (90%)] R_f 0.47. anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.20; H, 11.44.

1-[(*tert*-Butyldimethylsilyl)oxy]-4-(2-propyl)-1,5(*E*)-cyclodecadiene (8). Rearrangement of divinylcyclohexanol **5** was undertaken in an identical manner as detailed for cyclodecenone **7** except that after cooling to -78 °C, *tert*-butyldimethylsilyl chloride (155 mg, 1.04 mmol) dissolved in THF (0.75 mL) was introduced via syringe instead of ethanol. After an adequate reaction period to ensure complete silyl halide trapping (as monitored by TLC; typically 0.5 h at -78 °C), the excess potassium hydride was rapidly quenched with ethanol (1.0 mL) and processed as described for **7**. Solvent removal in vacuo gave a light yellow oil [R_f 0.72; ethyl acetate (5%)/petroleum ether (95%)] which proved highly unstable to further purification on chromatography sorbents or extended handling at room temperature (e.g., acquisition of ^{13}C NMR spectra). Upon treatment of crude silyl enol ether **8** obtained from such a reaction with tetra-*n*-butylammonium fluoride as the trihydrate (630 mg, 2.0 mmol) in THF (2.0 mL), cyclodecenone **7** was obtained in 80% yield from vinyl cyclohexanol **5** after purification on silica gel.

8: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 4.8–5.5 (2 H, m), 4.3 (1 H, m), 1.1–2.6 (12 H, m), 1.0 (6 H, d, J = 6 Hz), 0.9 (9 H, s), 0.1 (6 H, s); IR (NaCl, cm^{-1}) 2951, 2940, 2841, 1660, 1467, 1250, 840, 775.

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Registry No. 1 (isomer 1), 99885-71-9; 1 (isomer 2), 99945-84-3; 3, 99885-72-0; 4, 99885-73-1; 5 (isomer 1), 99885-74-2; 5 (isomer 2), 99945-85-4; 7, 99885-75-3; 8, 99885-76-4; 9, 99885-77-5; 10, 99885-78-6; 11, 99885-79-7; 12, 99885-80-0; 13, 99885-81-1; TBSCl, 18162-48-6; KH, 7693-26-7; I_2, 7553-56-2; $CH_3CH{=}CHCHO$, 4170-30-3; Bu_3SnH, 688-73-3; $CH_2{=}CHBr$, 593-60-2; 2-cyclohexenone, 930-68-7; cyclohexanone, 108-94-1.

Supplementary Material Available: Experimental details for the synthesis of *cis*- and *trans*-**1** (from cyclohexenone) and the synthesis of *cis*- and *trans*-**5** (from cyclohexanone) (8 pages). Ordering information is given on any current masthead page.

Synthesis of Aspartame via Asymmetric Hydrogenation of N-Protected (*Z*)-*N*-α-L-Aspartyl-Δ-phenylalanine Methyl Ester

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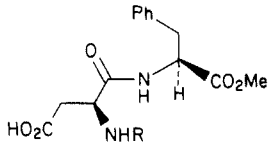
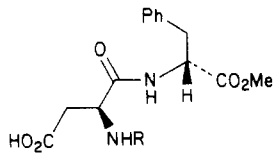
The usefulness of asymmetric hydrogenation of dehydropeptides in the preparation of peptides of high diastereoisomeric purity has been well established.[1] However, this synthetic principle has not been apparently applied to the preparation of the artificial sweetener aspartame (α-L-aspartyl-L-phenylalanine methyl ester)[2] (**1**), whose practical syntheses involve ring opening of N-protected L-aspartic anhydride with L-phenylalanine methyl ester.[3] This convergent approach suffers the drawback of the lack of regiospecificity. Indeed, minor amounts of the β-ring-opening product accompany the desired α-isomer, thus lowering the yield of incorporation of L-phenylalanine into **1**. Furthermore, until recently,[4] there was a considerable



1, R=H
2a, R=CHO
2b, R=COOCH$_2$Ph



3a, R=CHO
3b, R=COOCH$_2$Ph

difference in availability and price between the two amino acids used as starting materials. These circumstances

(1) Meyer, D.; Poulin, J.-C.; Kagan, H. B.; Levine-Pinto, H.; Morgat, J.-L.; Fromageot, P. *J. Org. Chem.* **1980**, *45*, 4680. Ojima, I.; Suzuki, T. *Tetrahedron Lett.* **1980**, *21*, 1239.

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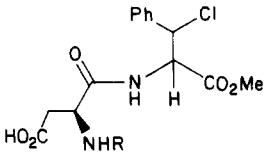
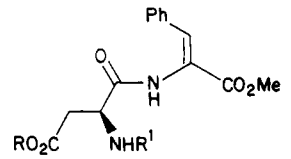
stimulated interest in new methods of preparation of the more valuable L-phenylalanine, including asymmetric hydrogenation[5] of (*Z*)-amidocinnamic acid derivatives, and studies[6] designed to increase the efficiency of incorporation of the latter amino acid into aspartame (**1**) through regiospecific coupling.

In this context, we now present a synthesis of aspartame (**1**) which formally overcomes the problem of the use of L-phenylalanine, being based (i) on the synthesis from readily accessible L-aspartic acid, benzaldehyde and glycine of N-protected dehydroaspartame (**5a,b**) and (ii) on its asymmetric hydrogenation in the presence of suitable chiral rhodium complex to a material containing over 90% of the L,L intermediate **2**, from which optically pure aspartame (**1**) is obtained upon deprotection and separation by crystallization from the accompanying L,D diastereoisomer.

The potential significance of this type of approach to **1** depends upon the accessibility of the unsaturated substrate. Dehydroaspartame is a known compound,[7] but its synthesis from L-aspartic acid and L-phenylalanine proceeds through multistep, low-yield sequence. Our approach to N-protected dehydroaspartame (**5a,b**) starts off from readily available L-aspartic acid, benzaldehyde, and glycine and follows a route similar to the one used in the preparation of aspartame (**1**). To this end, D,L-phenylserine



4a, R = CHO
4b, R = $COOCH_2Ph$



5a, R = H; R^1 = CHO
5b, R = H; R^1 = $COOCH_2Ph$
6, R = Me; R^1 = CHO

methyl ester hydrochloride, prepared[8] from benzaldehyde and glycine in 70% yield for the two steps, was converted into D,L-2-chlorophenylalanine methyl ester in 80% overall yield. Opening of *N*-formyl-L-aspartic anhydride with the above product in the presence of acetic acid afforded *N*-(*N*-formyl-α-L-aspartyl)-D,L-2-chlorophenylalanine methyl ester (**4a**), mp 148 °C, in 75% yield, and separated from ca. 15% of the β-isomer by crystallization from ethyl acetate. Product **4a**, upon dehydrohalogenation, afforded the required N-protected dehydroaspartame (**5a**) in 75% yield. From D,L-phenylserine methyl ester with *N*-formylaspartic anhydride we prepared also *N*-(*N*-formyl-α-L-aspartyl)-D,L-phenylserine methyl ester (**4a**, OH instead of Cl), but we were unable to convert it into the required **5a** under a variety of conditions.

Product **5a** presented a crystalline form not suitable for the X-ray single-crystal structure determination we needed in order to determinate double bond geometry and molecular shape. Accordingly, the above analysis was performed on the methyl ester **6**, mp 142 °C, prepared from **5a** upon treatment with ethereal diazomethane. Figure 1, showing a perspective view of the molecule, illustrates the results of the molecular structure determination.[9] The

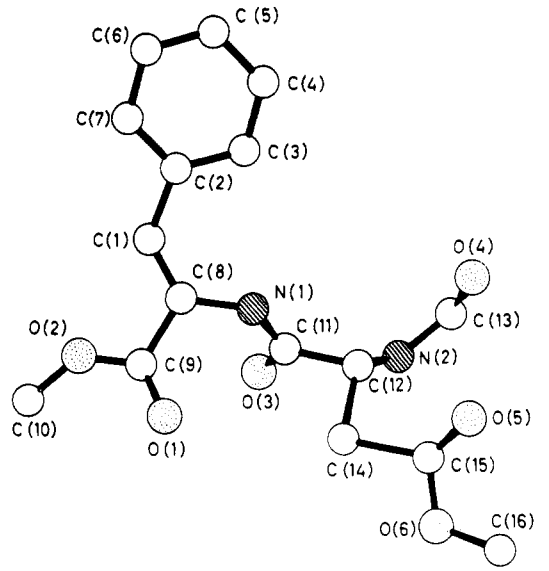


Figure 1. Perspective view of N^2-formyldehydroaspartame methyl ester **6**.

Table I. Steric Course of the Catalytic Hydrogenation of N^2-Formyldehydroaspartame 5a[a]

entry	catalyst	L,L-**2a**	L,D-**3a**	substrate/catalyst (w/w)	solv
1	10% Pd/C	45	55	30	EtOH
2	Rh-(*R*)-prophos[b]	90	10	60	THF
3	Rh-(*S,S*)-diop[c]	30	70	40	EtOH
4	Rh-PNNP[d]	70	30	60	MeOH

[a] Hydrogenation performed at 23 °C and 1 atm H_2. [b] Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6962. [c] Kagan, H. B.; Dang, T. P. *J. Chem. Soc. Chem. Commun.* **1971**, 481. [d] Fiorini, M.; Marcati, F.; Giongo, G. M. *J. Mol. Catal.* **1978**, *4*, 125.

C(8)–N(1) bond is cis to the C(1)–C(2) bond across the C(1)–C(8) double bond, with the intramolecular nonbonding distance N(1)···C(3) of 3.12 (1) Å. The phenyl ring is nearly coplanar to the plane defined by the sp^2 C(8) atom and its substituents. Both the nitrogen atoms appear to be sp^2 hydridized as evidenced by the quasi-coplanarity of the atoms N(1), C(8), and HN(1) and N(2), C(13), and HN(2), respectively, and by the sum of the bond angles around N(1) and N(2) very close to 360°. The shortening of the N(1)–C(11) and N(2)–C(13) bonds (1.337 (4) and 1.335 (4) Å) is also in agreement with $N_{sp^2} - C_{sp^2}$ partial double bond length. The crystal packing is dominated by an extended intra- and intermolecular hydrogen bond network of the type O···H–N and O···H–C.

The N^2-formyldehydroaspartame **5a** was submitted to the catalytic hydrogenation under the conditions and with the steric outcomes reported in Table I. The ratio between the L,L and L,D diastereoisomers **2a** and **3a** was

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(9) A colorless needle-shaped crystal was mounted on a NONIUS-CAD 4 automatic diffractometer (grapite monochromated, Cu Kα radiation, ϑ–2ϑ scan technique). From least-squares analysis on 18 reflections the compound appeared to be triclinic, space group *P*1 with a = 4.709 (10) Å, b = 9.135 (8) Å, c = 10.131 (8) Å, α = 101.9 (1)°, β = 96.95 (2)°, γ = 95.3 (2)°, V = 420 Å^3, Z = 1, $F(000)$ = 177, D_{calcd} 1.403 g cm^{-3}. The intensity of 2436 independent reflections were collected up to ϑ = 62°, of which 1750 with $I > 2.5\sigma(I)$ were considered observed and included in the refinement. The structure was solved by direct methods using MULTAN 80 (Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 80, University of York, England, and University of Louvain, Belgium, 1980) program and subsequent difference Fourier synthesis. Blocked full-matrix least-squares refinement, with anisotropic temperature factors for all non-H atoms and with the phenyl ring treated as rigid body, converged to R = 0.047 and R_W = 0.046.

determined on the crude hydrogenation mixture by ^1H NMR by measuring the relative intensities of the OMe signals due to the two diastereoisomers, which appear at 3.58 and 3.60 ppm, respectively, in Me_2SO-d_6, and by HPLC analysis, by comparison with authentic samples prepared from L-aspartic acid and L- and D-phenylalanine, respectively. The crude hydrogenation mixtures obtained in entries 2 and 4 were deformylated with methanolic hydrogen chloride to give, on neutralization and crystallization, aspartame (1), over 99.5% pure by HPLC, in 65% and 45% yield, respectively.

Similarly, starting from *N*-carbobenzoxy-L-aspartic anhydride, through the above sequence, N^2-carbobenzoxydehydroaspartame **5b**, mp 162 °C, α^{20}_D +32.6° (*c* 1, MeOH), was obtained. The latter material, on hydrogenation in the presence of (*R*)-prophos as a ligand of rhodium, afforded L,L-**2b** and L,D-**3b** in an over 90:10 ratio. Deprotection of the latter mixture by hydrogenolysis in the same pot with 10% Pd/C affords, on crystallization, aspartame (1), in 75% overall yield from **5b**.

The above results thus show the accessibility of L,L-aspartame (1) through a procedure involving as key step the generation of the L-phenylalanine moiety at the latest stages via asymmetric hydrogenation of N-protected α-L-aspartyl dehydropeptides. The method will be hardly competitive with the synthesis of 1 based on enzymatically produced L-phenylalanine as starting material, but it can be considered a further example of the significance to organic synthesis of the catalytic asymmetric hydrogenation.

Experimental Section

***N*-(*N*-Formyl-α-L-aspartyl)-D,L-2-chlorophenylalanine Methyl Ester (4a).** To a mixture of 230 g (1 mol) of D,L-phenylserine methyl ester hydrochloride in 400 mL of chloroform was added dropwise under stirring at room temperature 100 mL (1.43 mol) of $SOCl_2$. The reaction mixture was kept at room temperature for 12 h and then evaporated to dryness under vacuum at 40 °C. The residue separated from methanol–diethyl ether (1:1) to afford 210 g (85%) of D,L-2-chlorophenylalanine methyl ester hydrochloride, mp 175 °C. Anal. Calcd for $C_{10}H_{13}O_2NCl_2$: C, 47.99; H, 5.23; N, 5.60. Found: C, 47.82; H, 5.20; N, 5.63. A solution of 25 g (0.1 mol) of D,L-2-chlorophenylalanine methyl ester hydrochloride in 200 mL of H_2O was treated at 23 °C with 6.3 g (0.05 mol) of Na_2CO_3 in 400 mL of H_2O. After standing for 10 min the reaction mixture was extracted with ethyl acetate (2 × 50 mL), and the combined organic extracts, once dried over Na_2SO_4, were added dropwise under stirring at 0 °C to a solution of 14.3 g (0.1 mol) of *N*-formyl-L-aspartic anhydride (prepared by treating L-aspartic acid in 99% formic acid with acetic anhydride) in 50 mL of ethyl acetate containing 6 mL of acetic acid. After being stirred 2 h at 0 °C, the reaction mixture was cooled to −10 °C, thus separating 27 g (75%) of *N*-formyl-α-L-aspartyl-D,L-2-chlorophenylalanine methyl ester (**4a**): mp 148 °C; α^{20}_D −36° (*c* 1, MeOH). Anal. Calcd. for $C_{15}H_{17}O_6N_2Cl$: C, 50.49; H, 4.80; N, 7.85. Found: C, 50.42; H, 4.83; N, 7.81.

(*Z*)-*N*-(*N*-Formyl-α-L-aspartyl)-Δ-phenylalanine Methyl Ester (5a). To a stirred solution of 35.8 g (0.1 mol) of **4a** in 75 mL of THF was added portionwise at room temperature during 2 h 10.8 g (0.2 mol) of NaOMe. after 20 min the reaction mixture was diluted with 200 mL of ethyl acetate and treated under stirring with 200 mL of 10% HCl. After 10 min the organic phase was separated, washed with 50 mL of a 20% NaCl solution, dried over Na_2SO_4, and evaporated to dryness. The resiue was crystallized from ethyl acetate to give 24.2 g (75%) of **5a**: mp 155–157 °C; α^{20}_D +20.5° (*c* 1.1, MeOH). Anal. Calcd. for $C_{15}H_{16}O_6N_2$: C, 56.25; H, 5.04; N, 8.75. Found: C, 56.29; H, 5.01; N, 8.69. The methyl ester **6**, mp 142 °C, α^{20}_D +2.3° (*c* 1, MeOH)8 was obtained from methanol from the treatment of **5a** with CH_2N_2.

Aspartame (1). The hydrogenation experiments of **5a** were performed on 6.4 g (0.02 mol) in 10–15% solutions, under the conditions reported in Table I. At the end of the adsorption the reaction mixture was filtered (when required) and evaporated to dryness. The residue was taken up in ca. 40 mL of boiling water, concentrated until cloudy, and kept at 0 °C for 12 h. The precipitate was collected and deformylated by boiling for 30 min with 40 mL of 1 N HCl–methanol (1:6.5). The solution was neutralized with solid Na_2CO_3 and concentrated under vacuum to complete elimination of methanol, thus separating, on cooling to 0 °C, aspartame (1), mp 245–247 °C, α^{20}_D +31° (*c* 1, CH_3COOH), 99.5% by HPLC. The precipitated aspartame (1) from entries 2 and 4 weighs 3.66 (65%) and 2.35 g (45%), respectively.

Registry No. 1, 22839-47-0; **2a**, 33605-76-4; **2b**, 33605-72-0; **3a**, 99792-97-9; **4a**, 99792-96-8; **5a**, 100101-47-1; **5b**, 100101-48-2; **6**, 100020-80-2; D,L-phenylserine methyl ester hydrochloride, 80182-99-6; D,L-β-chlorophenylalanine methyl ester hydrochloride, 100020-81-3; *N*-formyl-L-aspartic anhydride, 33605-73-1; *N*-carbobenzoxy-L-aspartic anhydride, 4515-23-5.

Synthesis of Dihydroxy Thia Crown Ethers and Derivatization to Bicyclic Crown Compounds

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Crown ethers containing reactive groups are important intermediates for a variety of highly functionalized derivatives.[1] Despite this, thia crown ethers are not well-known[2] in spite of their excellent complexing ability toward transition-metal cations.[3] On the other hand, crown ethers having two or more functional groups are particularly interesting because of their potential application in the synthesis of bicyclic compounds.[4] We have recently reported a facile procedure for synthesizing aza crown ethers with two hydroxyl groups[5] and now describe the synthesis of a new class of thia crown ethers. These new thia crowns have two hydroxyl groups and can be converted into crown ethers having an oxathiane subcyclic unit.

The reaction of oligoethylene glycol diglycidyl ethers[6] (1) with sodium hydrosulfide in water at 60 °C for 3 h gave the dihydroxy thia crown ethers (**2**) in 52–63% yield (Scheme I). Ethanol and *tert*-butyl alcohol were also found to be desirable for this reaction, whereas the desired compounds were not obtained under the same reaction conditions when dioxane was used as solvent.

Although compounds **2** may be promising complexation agents for transition-metal cations,[3] they showed poor complexing ability toward alkali metal cations. However,

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