recovered zirconium species can be repeatedly used as the catalyst without any treatment.

Experimental Section

The melting points were determined on a Yanaco MP-52032 apparatus and are corrected. The IR spectra were taken with a JASCO A-202 spectrometer and the ^1H and ^{13}C NMR spectra were recorded on a JEOL PMX-60 and a Hitachi R-90H spectrometer, respectively. The GLC analyses were performed on a Yanaco G-1800 instrument with a 3 m × 2.5 mm column packed with 5% Silicone OV-7 on Chromosorb W.

Materials. Bis(cyclopentadienyl)zirconium dihydride (1) was prepared by the Wailes procedure:[1] mp 304–305 °C (lit.[1] mp 305 °C); IR (KBr) 3100, 1520, 1300, 1020, 840 cm^{-1}.

The compounds were of commercial grade, and the solvents were used after dehydration by conventional methods.

Reduction of Carbonyl Compounds by 1. Carbonyl compound (10 mmol), 2-propanol (20 mmol), and 1 (0.2 mmol) were placed in an autoclave (50 cm^3) under an argon atmosphere, and the reaction was carried out with mechanical shaking at 130 °C for 6 h. After removal of catalyst by filtration, the product was isolated by distillation or by MPLC on silica gel (hexane/ethyl acetate = 5:1 eluent). The spectral data of the reaction products agreed with those of authentic samples and literature values.[9,10]

Oxidation of Alcohols by 1. Alcohol (10 mmol), carbonyl compound (10 mmol), and 1 (0.2 mmol) were placed in an autoclave under an argon atmosphere. The reactions were carried out in a similar manner as above, and the products were identified by comparison of their spectral data with those of authentic samples and literature values.[11]

Registry No. Bis(cyclopentadienyl)zirconium dihydride, 37342-98-6; 2-propanone, 67-64-1; 4-methyl-2-pentanone, 108-10-1; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 2,6-dimethylcyclohexanone, 2816-57-1; acetophenone, 98-86-2; benzophenone, 119-61-9; 3-phenyl-2-propenal, 104-55-2; 3,5,5-trimethyl-2-cyclohexen-1-one, 78-59-1; 2-pentanone, 107-87-9; 2-propanol, 67-63-0; 4-methyl-2-pentanol, 108-11-2; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; 2,6-dimethylcyclohexanol, 5337-72-4; 1-phenylethanol, 98-85-1; diphenylmethanol, 91-01-0; 3-phenyl-2-propen-1-ol, 104-54-1; 3,5,5-trimethyl-2-cyclohexen-1-ol, 470-99-5; 2-pentanol, 6032-29-7; 1-butanol, 71-36-3; 2-butanol, 78-92-2; 1-octanol, 111-87-5; 2-octanol, 123-96-6; 1-dodecanol, 112-53-8; 1-octadecanol, 112-92-5; benzyl alcohol, 100-51-6; allyl alcohol, 107-18-6; geraniol, 106-24-1; butanal, 123-72-8; 2-butanone, 78-93-3; octanal, 124-13-0; 2-octanone, 111-13-7; dodecanal, 112-54-9; octadecanal, 638-66-4; benzaldehyde, 100-52-7; acrolein, 107-02-8; geranial, 141-27-5.

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Simple Access to Highly Enantiomerically Enriched (*S*)-3-Methyl-1-pentanol, (*S*)-3-Methyl-1-pentene, (2*R*,3*S*)-2-Deuterio-3-methyl-1-pentanol, and (2*S*,3*S*)-3-Methyl-2-pentanol from Natural L-Isoleucine

Volker Schurig,* Ulrich Leyrer, and Dorothee Wistuba

Institut für Organische Chemie, Universität Tübingen, D 74 Tübingen, West Germany

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The smallest chiral, aliphatic hydrocarbon residue, i.e., the *sec*-butyl group, occurs in essentially quantitative enantiomeric purity[1] in L-isoleucine [(2*S*,3*S*)-2-amino-3-methylpentanoic acid **1**]. As has been established by anomalous X-ray diffraction in the pioneering work of Trommel and Bijvoet[3] the absolute configuration of the *sec*-butyl group in unnatural D-isoleucine is *R*. We describe here the transformation of the "chiral carbon pool" compound L-isoleucine (**1**) into some small chiral molecules containing the (*S*)-*sec*-butyl group (cf. Scheme I). The configurational composition of the compounds prepared is unequivocal established by modern chromatographic and spectroscopic (^2H-NMR) methods.

According to Scheme I L-isoleucine (**1**) is transformed via diazotization (HCl, $NaNO_2$)[4,5] into (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (**2**). We have recently shown that this reaction proceeds with a high degree of stereointegrity, i.e., with 99.5% (!) of net retention of configuration at C-2, and with virtually no racemization at C-3 of the *sec*-butyl group.[2,5] Exhaustive reduction of **2** via route 1 furnishes the chiral primary alcohol (*S*)-3-methyl-1-pentanol (**3**) in 82% chemical yield.[5] This alcohol has previously been obtained by Pino et al.[6] via chain extension from (*S*)-2-methyl-1-butanol, and racemization to an unknown extent was believed to have occurred in their procedure. According to Pino et al.[6] the olefin (*S*)-3-methyl-1-pentene (**5**) (which was prepared from **3** on pyrolysis of the acetate **4**) was contaminated with 2.6% of 4-methyl-1-pentene arising from 3-methyl-1-butanol (occurring as contaminant of the starting alcohol 2-methyl-1-butanol).

In contrast, (*S*)-3-methyl-1-pentene (**5**) obtained from L-isoleucine **1** according to route 1 (Scheme I) is free of olefinic isomers. Its enantiomeric purity and that of the precursor, the alcohol **3**, has been established by two independent chromatographic methods. Thus, ee = 98.6% for (*S*)-3-methyl-1-pentene (**5**) has been determined by HPLC of the diastereomeric platinum olefin π complex *trans*-chloro-(*N*,*N*-dimethyl-D-phenylglycin)(η_2-(3*S*)-3-methyl-1-pentene)platinum(II).[7,8] In addition, a sample of **5** has been epoxidized with *m*-chloroperbenzoic acid to the diastereomeric oxiranes **8** (55%) and **9** (45%), which can be quantitatively resolved by complexation gas chromatography[5] on optically active nickel(II) bis(2-heptafluorobutyryl)-(1*S*)-4-methyl-thujan-3-onate).[9] For both **8** and **9** an enantiomeric purity of 98.8 ± 0.2% has been determined. Since no crystallization steps have been involved in the conversion of **3** to **5** and of **5** to **8** and **9**, respectively, it is obvious that the alcohol **3** and the olefin **5** were also *at least* 98.8% enantiomerically pure. By comparison of our specific rotation of (*S*)-3-methyl-1-pentene (**5**), i.e., $[\alpha]^{17}_D$ +33.72°, α^{17}_D +2.28° (l = 0.1 dm, neat), d^{17}_4 0.6703[6] (neat), ee = 98.8%, with that given by Pino et al.,[6] i.e. $[\alpha]^{17}_D$ +32.86°, it follows that their product had actually an enantiomeric purity of 96.4%, instead of an assumed purity of only 86%.[6]

Reduction of **2** via route 2 (Scheme I) furnishes the

(1) The configurational composition of a typical specimen of commercial L-isoleucine has been determined gas chromatographically on Chirasil-Val to 99.7% (2*S*,3*S*)-2-amino-3-methylpentanoic acid, 0.2% (2*S*,3*R*)-2-amino-3-methylpentanoic acid, 0.1% (2*R*,3*S*)-2-amino-3-methylpentanoic acid, and approximately 0% (2*R*,3*R*)-2-amino-3-methylpentanoic acid.[2]
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(3) Trommel, J.; Bijvoet, J. M. *Acta Crystallogr.* **1954**, *7*, 703–709.
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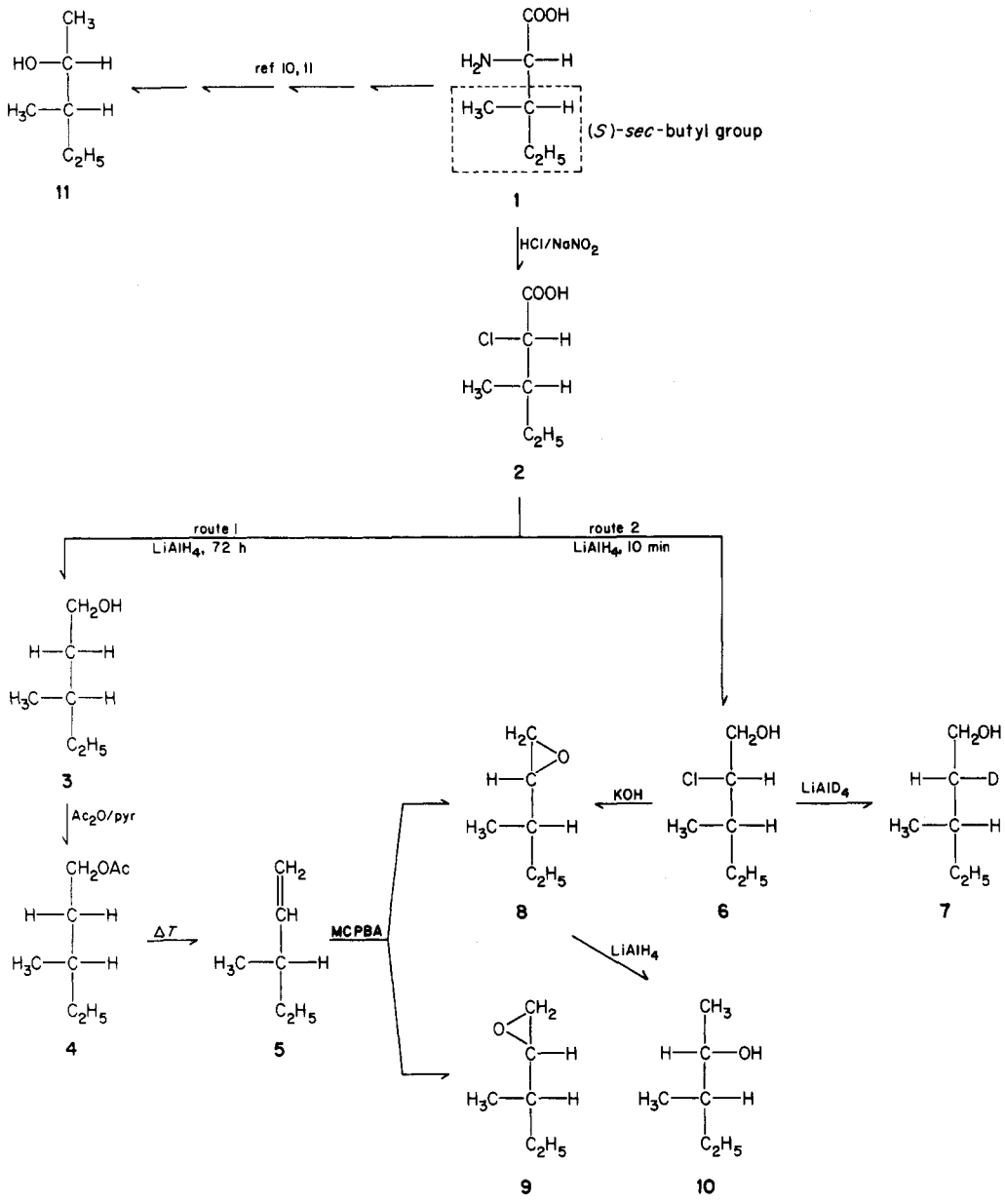
0022-3263/86/1951-0242$01.50/0

Scheme I



chlorohydrin **6** in 56% chemical yield.[5] Alkaline cyclization of **6** leads to (2*R*,3*S*)-1.2-epoxy-3-methylpentane (**8**) of high diastereomeric purity (de = 97.3%),[5] which can be transformed by treatment with $LiAlH_4$ into (2*S*,3*S*)-3-methyl-2-pentanol (**10**). This reduction proceeds with some epimerization at C-2 to give 9.25% (2*R*,3*S*)-3-methyl-2-pentanol (**11**) (cf. Figure 1). (2*R*,3*S*)-3-methyl-2-pentanol (**11**) may be obtained with overall retention of configuration at C-2 from L-isoleucine[10] via transformation into (2*S*,3*S*)-2-hydroxy-3-methyl-pentanoic acid (**12**), $LiAlH_4$ reduction of the THP-protected ethyl ester of **12** to give (2*S*,3*S*)-3-methyl-2-[(2-tetrahydropyranoyl)oxy]-1-pentanol (**13**), tosylation and $LiAlH_4$ reduction followed by acidification (overall yield in seven steps, 19%; configurational composition, 98.6% **11**, 1.4% **10**, de = 97.2 ± 1%, ee = 98.6 ± 1%).[11]

Deuterolysis of (2*S*,3*S*)-2-chloro-3-methyl-1-pentanol (**6**) with $LiAlD_4$ allows the incorporation of deuterium at C-2 yielding the diastereomeric primary alcohol **7**. The presence of the essentially enantiomerically pure (*S*)-*sec*-butyl group offers the opportunity to precisely determine the degree of stereospecificity of the nucleophilic displacement of chloride by deuteride which according to common belief proceeds with Walden inversion.[12,13] We found that the diastereomeric composition of 2-deuterio-3-methyl-1-pentanol (**7**) can be determined by ^2H NMR spectroscopy. A diastereomeric mixture of **7** obtained via route 2 (Scheme I) from a mixture of racemic isoleucine and *allo*-isoleucine showed distinct deuterium absorptions for the *erythro* and *threo* isomers in the ^2H NMR spectrum (cf. Figure 2A). (2*R*,3*S*)-2-Deuterio-3-methyl-1-pentanol (**6**) obtained from L-isoleucine via route 2 (Scheme I) displayed a diastereomeric purity of >96% (cf. Figure 2B). The intermediacy of the oxirane **8** in the conversion of the chlorohydrin **6** to the primary alcohol **7** can be discounted since no secondary alcohol has been detected during the transformation while treatment of **8** with $LiAlH_4$ exclusively leads to

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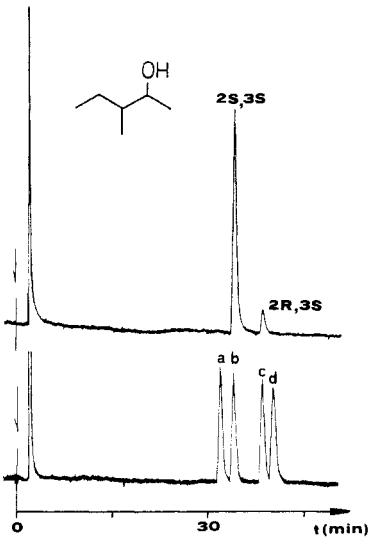

Figure 1. Complexation gas chromatography of 3-methyl-2-pentanol (Conditions: 40 m × 0.25 mm deactivated glass capillary coated with manganese(II) bis[3-(heptafluorobutyryl)-(1*R*)-camphorate] (0.156 m in OV 101);[14,15] carrier gas, 1.1 bar of N_2; split ratio 1:50; oven temperature, 55 °C). Top: enantiomeric and diastereomeric purity of (2*S*,3*S*)-3-methyl-2-pentanol (**10**). Bottom: enantiomer and diastereomer (*threo*/*erythro*) separation of 3-methyl-2-pentanol. Peak assignment, a (2*R*,3*R*)-**10**, b (2*S*,3*S*)-**10**, c (2*R*,3*S*)-**11**, and d (2*S*,3*R*)-**11**.

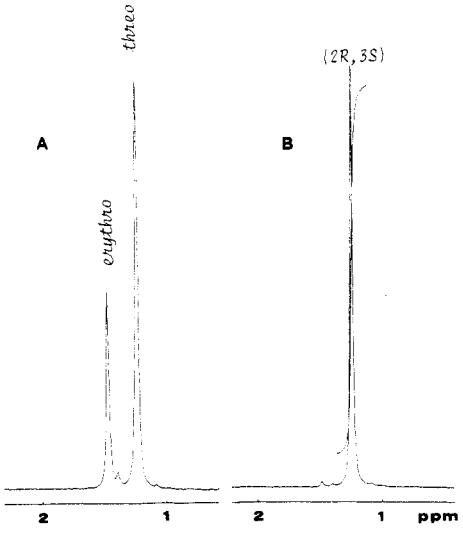

Figure 2. Broad-banded proton decoupled ^2H NMR spectra of 2-deuterio-3-methyl-1-pentanol (**7**). A: Diastereomeric mixture of racemic **7**. B: (2*R*,3*S*)-**7** obtained from L-isoleucine according to Scheme I. (Conditions: 22 °C, chemical shifts are relative to $CDCl_3$, added as an internal standard and set to 7.24 ppm. Samples were measured in CCl_4 with a Bruker-WM 400-MHz NMR spectrometer, which was locked internally on C_6F_6.)

the formation of **10** (vide supra). The results described here imply that enantiomerically (or diastereomerically) highly enriched 2-deuterio-1-alkanols may be obtained by $LiAlD_4$ treatment of enantiomerically (or diastereomerically) pure 2-chloro-1-alkanols.

In conclusion we have shown by employing modern gas chromatographic methods of enantiomer analysis that the configuration of the (*S*)-*sec*-butyl group of L-isoleucine is preserved in some basic chemical transformations summarized in Scheme I leading to enantiomerically highly enriched reaction products.

Experimental Section

(2*S*,3*S*)-2-Chloro-3-methylpentanoic Acid (2).[4,5] L-isoleucine[1] (100 g, 0.76 mol) was dissolved in 1800 mL of 5 N hydrochloric acid and the solution was cooled to 0 °C. A precooled (0 °C) solution of 125 g (1.8 mol) sodium nitrite in 150 mL of water was added dropwise at a rate of about 2 mL/min under vigorous stirring and efficient cooling so that the temperature of the reaction mixture was kept below 5 °C. After 5 h an additional 20 g (0.29 mol) of sodium nitrite in 25 mL of water was added. The reaction was allowed to warm to room temperature overnight. The solution was carefully evacuated to remove nitrous oxides. While the mixture was stirred 75 g of sodium carbonate was added carefully to prevent foaming. The reaction mixture was extracted with 3000 mL of ethyl acetate in four portions. The organic phase was dried over sodium sulfate and concentrated on a rotary evaporator. The residue was distilled two times to give respectively 80.2 g (70%) [first distillation at 79 °C (0.05 torr)] and 71.4 g (62.5%) [second distillation at 74-76 °C (0.4–0.6 torr)]: α^{20}_D −5.33° (*l* = 1 dm, neat), d^{20}_4 1.115, $[\alpha]^{20}_D$ −4.78° (neat) (diastereomeric purity; 98.3%); ^{13}C NMR (in $CDCl_3$) δ 179.9, 62.6, 38.8, 24.8, 15.8, 10.8. Anal. Calcd for $C_6H_{11}ClO_2$: C, 47.85; H, 7.36; Cl, 23.54. Found: C, 47.67; H, 7.17; Cl, 23.34.

(*S*)-3-Methyl-1-pentanol (3). This alcohol was prepared according to ref 5: yield, 82% (first distillation); ^{13}C NMR (in $CDCl_3$) δ 64.4, 37.5, 30.9, 29.4, 18.9, 11.0; α^{20}_D +0.656° (*l* = 0.1 dm, neat), d^{20}_4 0.8262,[6] $[\alpha]^{20}_D$ +7.94°[16] (neat) (ee > 98.8%). Anal. Calcd for $C_6H_{14}O$: C 70.52 H 13.81. Found: C, 70.26; H, 13.68.

(*S*)-3-Methylpentyl Acetate (4). This ester was prepared according to ref 6: ^{13}C NMR (in $CDCl_3$) δ 171.0, 62.9, 35.0, 31.3, 29.2, 20.9, 18.8, 11.0. Anal. Calcd for $C_8H_{16}O_2$: C, 66.64; H, 11.19. Found: C, 66.96; H, 11.26.

(*S*)-3-Methyl-1-pentene (5).[6] (*S*)-3-Methylpentyl 1-acetate (**4**) (8 g, 55.5 mmol) was pyrolyzed in a glass tube (120 × 1.5 cm) which was filled (from the bottom to the top) with 3-mm, 0.35-mm, 1-mm, and 2-mm i.d. glass spheres at 520–550 °C (oven, 25 × 4 cm i.d.) by using a stream of high purity grade nitrogen (2 mL/min). The acetic acid formed upon pyrolysis was neutralized with solid sodium carbonate and the olefin was collected in a cooled (−195 °C) trap; crude yield, 3.0 g (91%). The product was distilled at normal pressure using a Spaltrohr HMS 300 column (supplier, W. G. Fischer, D-5309 Meckenheim, Germany) to yield 1.7 g (48%) of (*S*)-3-methyl-1-pentene (**5**), bp 49–51 °C (760 torr). The optical rotation was measured with a sample distilled from CaH_2: α^{20}_D +2.26° (*l* = 0.1 dm, neat), α^{17}_D +2.28° (*l* = 0.1 dm, neat), d^{17}_4 0.6703,[6] $[\alpha]^{17}_D$ +33.72° (neat) ee ≥ 98.8%; ^{13}C NMR (in $CDCl_3$) δ 144.6, 112.8, 39.5, 29.3, 11.8, 11.5.

(2*R*,3*S*)-2-Deuterio-3-methyl-1-pentanol (7). A solution of 6.5 g (50 mmol) of (2*S*,3*S*)-2-chloro-3-methyl-1-pentanol (**6**) in diethyl ether was added to a suspension of 1.2 g (30 mmol) of lithium aluminum deuteride in diethyl ether under an atmosphere of nitrogen. The reaction mixture was refluxed for 144 h and afterwards was hydrolyzed with water and 15% potassium hydroxide. The residue was extracted with diethyl ether in a Soxhlet apparatus for 24 h. The ether layer was dried with sodium sulfate and concentrated and the residue distilled at 12 torr: yield, 3 g (58%); bp 57–58 °C (12 torr). The diastereomeric mixture of racemic **7** was prepared in the same way: ^2H NMR, the conditions are described in the legend to Figure 2; ^{13}C NMR (in $CDCl_3$) δ 77.3, 77.0, 76.7 (t, coupling with ^2H), 60.8, 30.9, 29.5, 19.0, 11.1.

(2*S*,3*S*)-3-Methyl-2-pentanol (10). A solution of 4 g (40 mmol) of (2*R*,3*S*)-1,2-epoxy-3-methyl-pentane (**8**)[5] (α^{20}_D +1.12° (*l* = 0.1 dm, neat), d^{20} 0.7598,[5] $[\alpha]^{20}_D$ +14.74°, de = 97.3 ± 0.5%, ee > 99.5%)[5] in 100 mL diethyl ether was added to a suspension of 1.6 g (42 mmol) lithium aluminum hydride in 100 mL of diethyl ether under an atmosphere of nitrogen. The reaction mixture was stirred overnight at room temperature and afterwards hydrolyzed with water and 2 N sulfuric acid. The residue was extracted five times with diethyl ether, and the combined organic phase was washed with saturated sodium hydrogen carbonate solution and with brine. The ether layer was dried with sodium sulfate and concentrated and the residue distilled at normal pressure: yield, 2.7 g (66%); bp 131–133 °C; ^{13}C NMR (in $CDCl_3$)

(16) The optical rotation of neat **3** is sensitive to traces of water. The sample was dried by percolation over active alumina. Literature data: α^{20}_D +6.75°, d^{20}_4 0.8262,[6] $[\alpha]^{20}_D$ +8.18° (neat),[5] $[\alpha]^{19}_D$ +8.24°,[6] $[\alpha]^{20}_D$ −8.5° (neat) (antipode), d^{20}_4 0.8227 (Mori, K.; Watanabe, H. *Tetrahedron* **1984**, *40*, 299–303), $[\alpha]^{20}_D$ −8.7° (neat) (antipode) (Rossi, R.; Carpita, A.; Chini, M. *Tetrahedron* **1985**, *41*, 627–633).

δ 70.9, 41.5, 25.2, 20.1, 13.6, 11.6; configurational composition (cf. Figure 2), (2S,3S)-10 90.75%, (2R,3R)-10 <0.5%, (2R,3S)-11 9.25%, (2S,3R)-11 <0.5%; α^{20}_D −0.837° (l = 0.1 dm, neat), $[\alpha]^{20}_D$ −10.85° (c 1.18, anhydrous methanol), de = 81.5%, ee > 99.0%.

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Crystal Structures of Monensin B Lithium and Silver Salts

David M. Walba,*[1a] Mark Hermsmeier, R. Curtis Haltiwanger, and Jan H. Noordik[1b]

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

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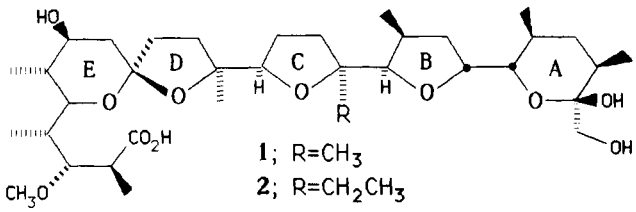
Monensin B (MonB, 1) is one of the large group of internally charge-compensating ionophores known to possess interesting biological and physicochemical properties.[2]



MonB and the closely related Monensin A (2) show selectivity for sodium in complexation experiments in methanol[3]—a relatively rare selectivity profile for the naturally occurring monocarboxylic acid ionophores.

One approach to understanding the complexation properties of hosts such as the monensins involves analysis of single-crystal X-ray structures of various complexes. In a very interesting and provocative study, Duax has compared conformations in the crystal of various complexes of monensin A with the free acid.[4] It was found that the major conformational adjustments made by Monensin A when forced to accomodate cations in different environments involved changes in the torsion angles of bonds near the C-ring of the ionophore. Unfortunately, no three of the monensin A complexes studied to date shows the same pattern of hydration in the crystal, though it seems reasonable that the best comparison between crystal conformations would involve complexes with similar hydration.

We have succeeded in obtaining X-ray crystal data for Monensin B Li^+ ($MonB^-Li^+$) and Ag^+ salts. The crystal

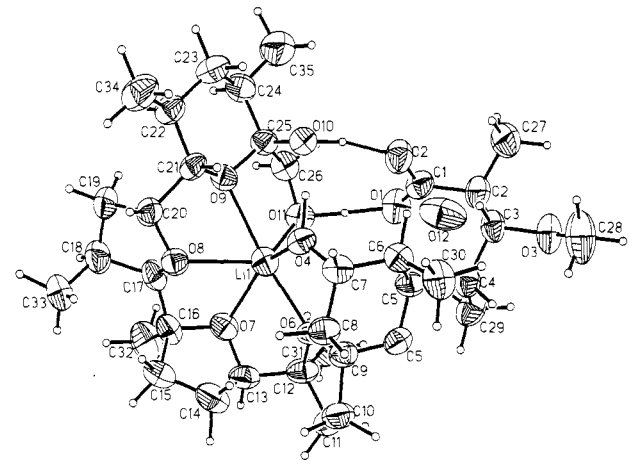


Figure 1. Crystal structure of monensin B lithium salt monohydrate showing the atomic numbering scheme utilized in the crystallography.

Table I. Atomic Coordinates for Monensin B Silver Salt

atom	x/a	y/b	z/c
Ag(1)	0.44221 (4)	0.10066 (4)	0.28690 (3)
O(1)	0.4658 (5)	−0.0046 (4)	0.1093 (3)
O(2)	0.4366 (5)	0.1439 (4)	0.1009 (3)
O(3)	0.7312 (4)	0.1321 (3)	−0.0125 (2)
O(4)	0.4910 (4)	0.2501 (4)	0.2429 (3)
O(5)	0.7538 (3)	0.1532 (3)	0.2190 (3)
O(6)	0.6356 (3)	0.1100 (4)	0.3011 (2)
O(7)	0.5093 (4)	0.0156 (3)	0.3897 (2)
O(8)	0.3535 (4)	0.1602 (3)	0.3953 (2)
O(9)	0.2342 (3)	0.1254 (3)	0.2872 (3)
O(10)	0.2836 (4)	0.1824 (3)	0.1861 (2)
O(11)	0.3503 (4)	0.0049 (3)	0.2147 (3)
O(12)	0.5410 (8)	−0.1633 (5)	0.0580 (5)
C(1)	0.4832 (6)	0.0713 (8)	0.0860 (4)
C(2)	0.5674 (7)	0.0764 (5)	0.0282 (3)
C(3)	0.6583 (6)	0.1434 (5)	0.0428 (3)
C(4)	0.7275 (6)	0.1316 (5)	0.1046 (4)
C(5)	0.6749 (6)	0.1660 (5)	0.1664 (4)
C(6)	0.6419 (6)	0.2653 (5)	0.1659 (4)
C(7)	0.5940 (6)	0.2922 (5)	0.2313 (4)
C(8)	0.6684 (6)	0.2698 (5)	0.2865 (4)
C(9)	0.7156 (6)	0.1738 (5)	0.2840 (5)
C(10)	0.8092 (6)	0.1565 (6)	0.3301 (4)
C(11)	0.8023 (6)	0.0565 (6)	0.3421 (4)
C(12)	0.6816 (6)	0.0354 (5)	0.3351 (4)
C(13)	0.6223 (6)	0.0288 (6)	0.4015 (4)
C(14)	0.6253 (6)	0.1132 (7)	0.4443 (4)
C(15)	0.5217 (6)	0.1053 (6)	0.4860 (4)
C(16)	0.4481 (7)	0.0369 (5)	0.4484 (3)
C(17)	0.3413 (6)	0.0750 (5)	0.4261 (4)
C(18)	0.2476 (6)	0.0884 (6)	0.4728 (4)
C(19)	0.1713 (7)	0.1410 (6)	0.4279 (4)
C(20)	0.2485 (5)	0.1996 (5)	0.3894 (4)
C(21)	0.2190 (6)	0.2138 (5)	0.3170 (4)
C(22)	0.1035 (6)	0.2456 (6)	0.3065 (4)
C(23)	0.0763 (6)	0.2438 (6)	0.2346 (4)
C(24)	0.0960 (6)	0.1460 (6)	0.2066 (4)
C(25)	0.2149 (5)	0.1208 (5)	0.2174 (4)
C(26)	0.2392 (6)	0.0271 (5)	0.2005 (4)
C(27)	0.5079 (7)	0.0970 (7)	−0.0349 (4)
C(28)	0.7891 (8)	0.2120 (6)	−0.0284 (5)
C(29)	0.7581 (7)	0.0286 (5)	0.1134 (4)
C(30)	0.7368 (7)	0.3263 (6)	0.1490 (5)
C(31)	0.6615 (7)	−0.0483 (5)	0.2978 (5)
C(32)	0.4328 (8)	−0.0500 (6)	0.4654 (4)
C(33)	0.2732 (8)	0.1396 (7)	0.5350 (4)
C(34)	0.0864 (8)	0.3407 (6)	0.3304 (6)
C(35)	0.058 (1)	0.144 (1)	0.1413 (6)

(1) (a) Dreyfus Teacher-Scholar, 1983–1985. (b) Permanent address: Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

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