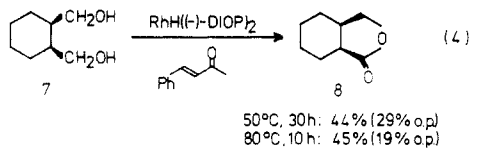

as a transition metal complex catalyzed counterpart of enzymatic reaction.[11]

Experimental Section

Proton NMR spectra were taken on a Hitachi R-40 (90 MHz) spectrometer or a JEOL JNM-GX400 (400 MHz) spectrometer using chloroform-*d* as a solvent. IR spectra were taken on a Shimadzu IR-400 spectrophotometer as neat film. Analyses by gas chromatography were performed on a Shimadzu GC-6AM instrument equipped with a frame ionization detector and a Shimadzu Chromatopac C-E1B calculating integrator using an adequate internal standard. A 2-m steel column filled with 60/80 mesh Uniport HB with 2% carbowax 40M was used. A Hitachi 163 instrument fitted with a thermal conductivity detector was used for preparative GC.

All of the diols were prepared by $LiAlH_4$ reduction of corresponding dicarboxylic acids, diesters, or cyclic anhydrides. $RhH(PPh_3)_4$,[12] $RhCl(PPh_3)_3$,[13] $RhH(CO)(PPh_3)_3$,[14] and $RhH((-)\text{-DIOP})_2$[15] were prepared according to the literature methods. Toluene was dried over sodium, distilled, and stored under argon. Other chemicals were reagent-grade commercial products.

An Example of Catalytic Regioselective Dehydrogenation of a Diol. A mixture of 2,2-dimethyl-1,4-butanediol (**1a**) (1.0 mmol) and 4-phenyl-3-buten-2-one (2.0 mmol) was dissolved in toluene (5 ml) under argon, and $RhH(PPh_3)_4$ (0.04 mmol) was added in one portion. Resulting yellow solution was stirred for 10 h at 50 °C. GC analysis of the reaction mixture indicated that the dehydrogenation of the diol gave a mixture of dihydro-4,4-dimethyl-2(3*H*)-furanone (**2a**) and dihydro-3,3-dimethyl-2-(3*H*)-furanone (**3a**) in the ratio of 98:2 in 95% yield. The structure of the products were fully characterized by ^1H NMR and IR spectra after purification by preparative GC.

An Example of Catalytic Enantioselective Dehydrogenation of a Diol. A mixture of *cis*-1,2-bis(hydroxymethyl)-cyclohexane (**7**) (5 mmol) and 4-phenyl-3-buten-2-one was dissolved in toluene (25 mL) under argon, $RhH((-)\text{-DIOP})_2$ (0.2 mmol) was added in one portion, and the solution was stirred for 30 h at 50 °C. The solvent was evaporated off, and the product was purified by column chromatography (silica gel, 6:4 ether–hexane) followed by bulb-to-bulb distillation to give (3_aR,7_a*S*)-hexahydro-1(3*H*)-isobenzofuranone (**8**) (44%), and the optical yield was determined to be 29% from its optical rotation.[11b]

Acknowledgment. This work was supported by Grants in Aid for Developmental Scientific Research from the Ministry of Education of Japan (58550556).

Registry No. **1a**, 32812-23-0; **1b**, 2938-98-9; **1c**, 39497-66-0; **1d**, 6837-05-4; **1e**, 13942-68-2; **1f**, 63842-86-4; **1g**, 3121-82-2; **1h**, 42856-62-2; **1i**, 101999-42-2; **2a**, 13861-97-7; **2b**, 1679-49-8; **2c**, 10547-88-3; **2d**, 1008-73-7; **2e**, 20514-72-1; **2f**, 101999-37-5; **2g**, 1679-55-6; **2h**, 3123-98-6; **2i**, 62618-74-0; **3a**, 3709-08-8; **3b**, 1679-47-6; **3c**, 1608-63-5; **3d**, 6836-98-2; **3e**, 25600-25-3; **3f**, 25600-27-5; **3g**, 4830-05-1; **3h**, 10603-03-9; **3i**, 13019-37-9; **5**, 4457-71-0; (±)-**6**, 62989-38-2; **7**, 15753-50-1; **8**, 65376-02-5; $RhH(PPh_3)_4$, 18284-36-1; $RhH((-)\text{-DIOP})_2$, 102490-04-0; $PhCH{=}CHCOCH_3$, 122-57-6.

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Stereoselective Synthesis of the Novel Bisnorditerpene Grindelistrictic Acid, Isolated from *Grindelia stricta*

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Most of the diterpenes isolated from plants of the genus *Grindelia* are structurally related to grindelic acid (**1a**)[1] (Chart I). Recently, however, a new type of terpenoids carrying a spiroketal moiety, namely strictanonic acid (**2a**) and the bisnorditerpene grindelistrictic acid (**3a**), were isolated in very small amounts from *G. stricta*.[2] Considerable attention has been given to the natural products containing spiroketal moieties, from the point of view of biological and synthetic interests.[3-5] In addition, since the **2a** and **3a** structures were proposed only on the basis of NMR data, unambiguous syntheses were needed for their confirmation. We have already succeeded in the synthesis of **2b**,[6] and now, we wish to report the stereoselective synthesis of **3b**.

We examined the synthesis of **3b** via the intramolecular ketalization of the C-18 precursor **4**, which could be obtained by oxidative cleavage of ester **5a**,[7] the reduction product of the known ketol **6**.[8] The latter possesses three of the four chiral centers present in **3b**.

For the preparation of **6** we used a three-step procedure, involving the reductive cleavage of **1a** to give **7**, followed by methylation and Jones oxidation to afford **6** in a 43% overall yield. Sodium borohydride reduction of **6** produced mainly the equatorial allylic alcohol **5a**, as shown by the half-band width of its H-7 signal. However, when **5a** was submitted to ozonolysis, compound **8** was obtained, after workup, as an epimeric mixture at C-7. The production of **8** indicated, in agreement with our previous experience in the synthesis of **2b**,[6] that the keto group formed by cleavage of the carbon–carbon double bond is immediately trapped as an intramolecular ketal, which then precludes the further cleavage of the α-ketol moiety.

In order to avoid the formation of **8** during the ozonolysis workup, we protected the allylic alcohol as an acetate (**5a** → **5b**).[9] In this case **5b** afforded **9** in 77% yield. The removal of the extra two-carbon unit of **9** would require the hydrolysis of the acetate under conditions that would favor cleavage over ketalization. The use of mild alkaline conditions in the presence of the cleaving agent ($NaIO_4$,

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(9) Compound **5b** was also prepared by direct oxidation of **1b**, according to the procedure described in ref 8, followed by $NaBH_4$ reduction and acetylation, in an overall yield of 40%.

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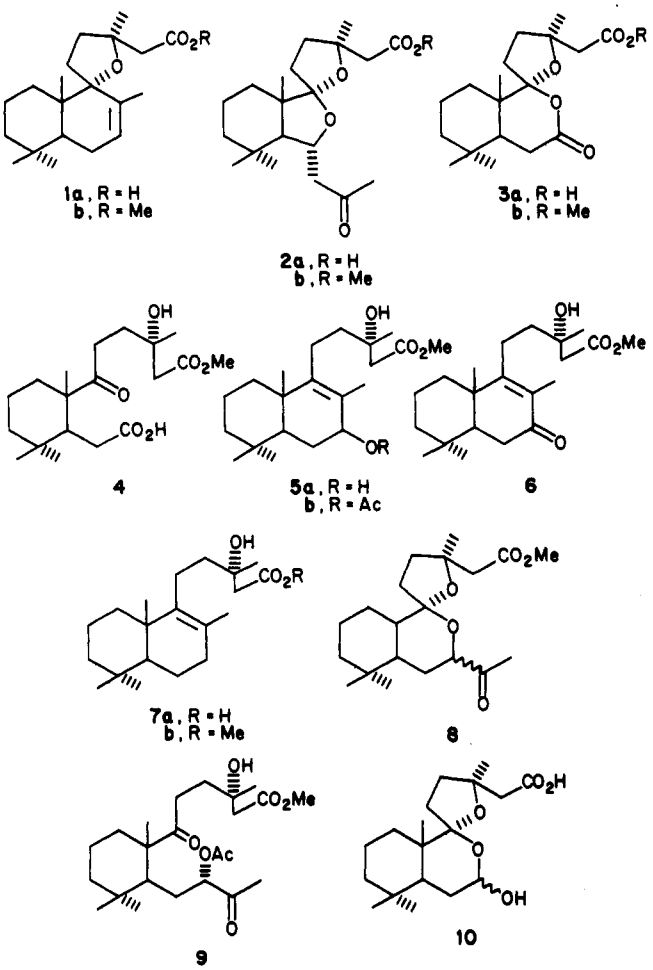
Table I. Carbon Shifts[a] of Compounds Studied

C	3b	5a	5b[b]	6	7b	9[c]
C-1	32.3	39.8	39.5	39.7	36.9	35.2
C-2	18.0	18.6	18.6	18.3	18.9	18.0
C-3	40.8	41.3	41.4	41.0	41.9	41.0
C-4	32.4	32.7	32.8	32.7	33.5	33.9
C-5	40.7	49.7	49.5	49.9	51.7	44.5
C-6	31.2	29.6	25.6	34.8	21.9	27.4
C-7	170.8	72.6	75.3	199.8	33.5	78.0
C-8		128.6	124.8	129.7	125.7	205.2
C-9	118.4	143.5	146.1	167.7	139.7	216.3
C-10	38.3	36.7	36.5	35.5	39.0	52.2
C-11	28.8	22.1	22.1	23.4	18.9	31.8
C-12	34.8	41.0	40.9	41.0	41.7	36.5
C-13	84.3	70.9	70.9	70.7	71.0	70.1
C-14	46.9	44.3	44.3	44.3	44.3	45.4
C-15	171.8	173.0	173.0	172.6	173.2	172.7
C-16	25.7	26.2	26.5	26.1	26.3	26.3
C-17		14.3	14.4	10.8	20.0	25.8
C-18	31.9	32.8	32.8	32.2	33.1	33.8
C-19	20.7	21.4	21.4	21.0	21.5	22.5
C-20	16.2	20.0	19.8	17.8	19.2	17.2
OMe	51.3	51.4	51.4	51.4	51.3	51.4

[a] In ppm. [b] The acetyl CO and Me shifts are 170.9 and 21.1 ppm, respectively. [c] The acetyl CO and Me shifts are 170.7 and 20.4 ppm, respectively.

Chart I



K_2CO_3 in *t*-BuOH, H_2O) afforded the ketal–hemiketal **10** as an epimeric mixture, as shown by the ^1H NMR signals of the H-7 (δ 5.10 and 5.44 as doublet of doublets). Finally, methylation of **10** with diazomethane followed by oxidation with pyridinium chlorochromate adsorbed on neutral alumina afforded **3b** in 75% overall yield from **9**

Although we have no control on the stereochemistry at C-9 in this synthetic sequence, it seemed reasonable to assume that the stereocontrol in the ketalization would be dominated by the stereoelectronic effects[10] and, therefore, would produce the C-9 stereochemistry as in the natural product. The ^1H NMR (400 MHz) and mass spectral data of synthetic **3b** are coincident with those of the natural product, and furthermore, the ^{13}C NMR spectrum shows the expected signals supporting the proposed structure. The carbon shifts for **3b** and the synthetic intermediates **5a**, **5b**, **6**, **7b**, and **9** are listed in Table I.

Experimental Section

Infrared spectra were measured with a Beckman Acculab 8 spectrophotometer as films unless specified otherwise. NMR spectra were recorded on a Bruker WP 80 SY spectrometer in $CDCl_3$ solutions. The ^1H NMR spectra were measured at 80.13 MHz, Me_4Si was used as an internal standard, and chemical shifts are expressed in δ; J and half-band widths ($W_{1/2}$) are given in hertz. The ^{13}C NMR spectra were measured at 20.15 MHz, and the δ values are in parts per million downfield from Me_4Si [$\delta(Me_4Si) = \delta(CDCl_3) + 76.9$]. Silica gel GF_{254} (Type 60) was utilized for thin-layer plates (TLC), and spots were visualized by staining with anisaldehyde–sulfuric acid.[11]

Compound 7b. In a 100-mL three-necked round-bottom flask equipped with magnetic stirrer, dry ice condenser, and pressure-equalizing addition funnel was placed a solution of grindelic acid (**1a**, 100 mg, 0.31 mmol) in anhydrous Et_2O (15 mL), NaH (15.7 mg, 55%, 0.38 mmol) was added under dry N_2, and the mixture was stirred for 30 min. Ammonia (15 mL) was then condensed, and the mixture was cooled (–60 °C). Sodium (36 mg, 1.55 mmol) was added in small portions in a stream of dry N_2. The resulting blue-green solution was stirred for 4 h in refluxing ammonia (–34 °C). *t*-BuOH was then added until complete decoloration. The ammonia was allowed to evaporate and the residue was taken up in H_2O (15 mL). The mixture was brought to pH 3 (10% HCl) and then extracted with Et_2O (2 × 15 mL). The combined Et_2O extract was washed with brine until neutral and dried (Na_2SO_4). The filtered solution was cooled (0 °C) and treated with an excess of ethereal solution of CH_2N_2. The excess of CH_2N_2 was destroyed (AcOH) and the solvent evaporated. The residue (90 mg) was purified by column chromatography over silica gel (7 g), with hexane and increasing amounts of EtOAc affording methyl grindelate (**1b**, 10 mg) and compound **7b** (70 mg, 70%)

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as a colorless oil: $[\alpha]_D$ +28.6° (c 1.03, $CHCl_3$); IR ν 3500, 2950, 2870, 1740, 1460, 1450, 1380, 1350, 1220, 1180, 1120 cm^{-1}; ^1H NMR δ 0.83, 0.88, 0.94 (C-4 and C-10 Me), 1.26 (C-13 Me), 1.55 (C-8 Me), 2.50 (s, H-14), 3.70 (s, OMe); mass spectrum, m/e (relative intensity) 336 (M^+, 1), 335 (8), 317 (6), 304 (3), 285 (2), 277 (5), 259 (6), 243 (8), 233 (22), 226 (70), 210 (14), 205 (25), 197 (12), 189 (16), 177 (24), 163 (25), 147 (28), 135 (100), 123 (80), 117 (75), 109 (90), 95 (82), 69 (73), 43 (87); found for M^+ m/e 336.2710 ($C_{21}H_{36}O_3$ requires m/e 336.2664).

Compound 6. A solution of **7b** (118 mg, 0.35 mmol) in acetone (2.5 mL) was stirred overnight, in the cold (0 °C), with Jones' reagent (1 mL). Usual workup gave an oily residue (102 mg), which was purified by silica gel column chromatography (5 g, hexane and hexane–EtOAc), affording **6** (71 mg, 0.21 mmol, 60%) as a colorless oil: $[\alpha]_D$ +16.3° (c 2.5, $CHCl_3$); IR ν 3500, 2980–2860, 1730, 1660, 1610, 1450, 1380, 1340, 1210, 1090, 920, 740 cm^{-1}; ^1H NMR δ 0.88, 0.92, 1.10 (C-4 and C-10 Me), 1.30 (C-13 Me), 1.75 (C-8 Me), 2.53 (s, H-14), 3.73 (s, OMe); mass spectrum, m/e (relative intensity) 350 (M^+, 7), 331 (13), 316 (5), 300 (2), 284 (2), 272 (1), 258 (4), 234 (16), 232 (24), 227 (41), 225 (100), 205 (18), 176 (17), 161 (13), 152 (15), 134 (29), 133 (19), 123 (14), 116 (32), 104 (18), 43 (58); found for M^+ m/e 350.2455 ($C_{21}H_{34}O_4$ requires m/e 350.2457).

Compound 5a. To a solution of **6** (70 mg, 0.2 mmol) in MeOH (5 mL) was added $NaBH_4$ (10 mg, 0.26 mmol), the mixture was stirred at room temperature, and additional amounts of $NaBH_4$ (10 mg, 0.26 mmol each) were added every hour. The progress of the reaction was monitored by TLC. After 3 h, the reaction was complete. Brine (10 mL) was added, and the mixture was extracted with Et_2O (2 × 15 mL). The combined Et_2O extract was washed with brine (2 × 10 mL), dried (Na_2SO_4), and evaporated, affording an oily residue (65 mg, 0.18 mmol, 90%) of compound **5a**: $[\alpha]_D$ +39.3° (c 1.14, $CHCl_3$); IR ν 3400, 2980–2850, 1735, 1450, 1380, 1340, 1210, 1110, 1020, 920, 740 cm^{-1}; ^1H NMR δ 0.85, 0.88, 1.01 (C-4 and C-10 Me), 1.27 (C-13 Me), 1.66 (C-8 Me), 2.50 (s, H-14), 3.71 (s, OMe), 4.01 (m, $W_{1/2}$ = 25.6 Hz, H-7); mass spectrum, m/e (relative intensity) 352 (M^+, 30), 350 (32), 334 (15), 318 (17), 315 (20), 302 (19), 300 (21), 227 (13), 219 (50), 210 (28), 206 (13), 189 (12), 176 (9), 163 (8), 150 (9), 135 (15), 117 (18), 109 (100), 43 (60); found for M^+ m/e 352.2653 ($C_{21}H_{36}O_4$ requires m/e 352.2613).

Compound 5b. A solution of compound **5a** (80 mg, 0.23 mmol) and Ac_2O (0.2 mL) in pyridine (2 mL) was stirred overnight at room temperature. The mixture was then poured into ice and extracted with Et_2O (2 × 10 mL). The Et_2O solution was washed with 2 N HCl (2 × 10 mL) and brine (until neutral), dried (Na_2SO_4), and evaporated. Flash chromatography over silica gel (hexane and hexane–EtOAc) afforded **5b** (74 mg, 0.19 mmol, 83%): $[\alpha]_D$ +31.4° (c 0.6, $CHCl_3$); IR ν 3500, 2930, 1740, 1730, 1450, 1380, 1250, 1030 cm^{-1}; ^1H NMR δ 0.83, 0.88, 1.03 (C-4 and C-10 Me), 1.26 (C-13 Me), 1.51 (C-8 Me), 2.07 (CH_3COO-), 2.50 (s, H-14), 3.71 (s, OMe), 5.32 (t, J = 8 Hz, H-7); mass spectrum, m/e (relative intensity) 394 (M^+, 2), 376 (2), 375 (6), 374 (2), 365 (1), 352 (1), 335 (6), 334 (6), 315 (10), 301 (8), 262 (12), 220 (100), 210 (85), 189 (38), 173 (17), 159 (15), 147 (15), 133 (22), 119 (51), 117 (62), 109 (36), 105 (18), 43 (51); found for M^+ m/e 394.2788 ($C_{23}H_{38}O_5$ requires m/e 394.2719).

Compound 9. A stream of O_2/O_3 was bubbled through a cold (−30 °C) solution of **5b** (50 mg, 0.13 mmol) in a 1:1 mixture of CH_2Cl_2–MeOH (4 mL) during 2 h. The excess of O_3 was then displaced by a N_2 stream, and the mixture was treated with $(MeO)_3P$ (0.1 mL) at room temperature for 30 min. The solvent was evaporated, and the residue (55 mg) was purified by preparative TLC (silica gel, 70:30 hexane–EtOAc), yielding **9** (43 mg, 0.1 mmol, 77%): $[\alpha]_D$ −9.47° (c 0.8, $CHCl_3$); IR ν 3450, 3000–2900, 1760–1720, 1450, 1380, 1230, 1110, 1060, 920, 750 cm^{-1}; ^1H NMR δ 0.87, 0.95, 1.23 (C-4, C-10, and C-13 Me), 2.12 (s, 6 H, C-8 Me and CH_3COO), 2.50 (s, H-14), 2.57–2.85 (m, 2 H, H-11), 3.72 (s, OMe), 4.50 (dd, J = 5.8 and 8.3 Hz, H-7); mass spectrum, m/e (relative intensity) 382 ($M^+ - CO_2$, 5), 364 (6), 322 (20), 304 (3), 291 (5), 265 (7), 249 (18), 227 (21), 195 (19), 167 (25), 141 (28), 123 (85), 109 (100), 95 (55), 69 (83), 43 (65).

Compound 3b. A solution of **9** (70 mg, 0.16 mmol), K_2CO_3 (75 mg, 0.54 mmol), and $NaIO_4$ (150 mg, 0.70 mmol) in a 1:1 t-BuOH–H_2O mixture (10 mL) was stirred at room temperature. Additional amounts of K_2CO_3 and $NaIO_4$ was added after 24 and 48 h. After 72 h, the solvent was evaporated, and the residue was taken up in H_2O (5 mL). The mixture was saturated with NaCl, brought to pH 3 (10% HCl), and extracted with Et_2O (2 × 15 mL). The combined Et_2O extract was washed with brine until neutral and dried (Na_2SO_4). After being filtered, it was treated with excess ethereal solution of CH_2N_2 at 0 °C for 30 min. The solvent was evaporated, and the residue was redissolved in CH_2Cl_2 (5 mL) and treated with PCC/Al_2O_3[12] (160 mg). The mixture was stirred at room temperature overnight. It was then filtered through Celite, and the solvent was evaporated. The residue (53 mg) was purified by a silica gel column chromatography (3 g, hexane and hexane–EtOAc) to afford **3b** (42 mg, 0.12 mmol, 75% from **9**) as an oil: $[\alpha]_D$ −26.1 (c 0.8, $CHCl_3$); IR ν 2960, 1750, 1740, 1450, 1340, 1270, 1250, 1200, 960, 900, 780 cm^{-1}; ^1H NMR δ 0.88, 1.03 (C-4 and C-10 Me), 1.30 (C-13 Me), 2.37–2.57 (m, 2 H, H-6), 2.72 (s, H-14), 3.66 (s, OMe); mass spectrum, m/e (relative intensity) 294 ($M^+ - CO_2$, 9), 265 (6), 247 (4), 223 (15), 197 (21), 173 (51), 165 (18), 155 (23), 123 (35), 109 (100), 95 (39), 69 (54), 55 (26), 43 (19).

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Registry No. **1a**, 1438-57-9; **1b**, 1438-58-0; **3a**, 81916-08-7; **3b**, 81916-38-3; **5a**, 102505-49-7; **5b**, 102505-51-1; **6**, 102505-48-6; **7a**, 102505-54-4; **7b**, 102505-47-5; **8** (isomer 1), 102505-50-0; **8** (isomer 2), 102572-03-2; **9**, 102505-52-2; **10** (isomer 1), 102505-53-3; **10** (isomer 2), 102572-04-3; **10** (methyl ester) (isomer 1), 102505-55-5; **10** (methyl ester) (isomer 2), 102572-05-4.

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Nafion-H† Catalyzed Reductive Cleavage of Acetals and Ketals to Ethers with Triethylsilane[1]

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Acetals and ketals are protected carbonyl compounds which can be reduced to either ethers or hydrocarbons under a variety of conditions.[2] Noyori and co-workers[3] have shown that acetals can be conveniently reduced to ethers with triethyl- or trimethylsilane catalyzed by trimethylsilyl trifluoromethanesulfonate. More recently Mukaiyama and co-workers have used[4] trityl perchlorate as a catalyst to convert carbonyl compounds to symmetrical and unsymmetrical ethers with triethylsilane. Over the years we have shown that Nafion-H[5] a superacidic perfluororesinsulfonic acid is a convenient catalyst for a variety of acid-catalyzed synthetic transformations. The selectivity, high catalytic activity, and ease of regeneration frequently makes Nafion-H the acid catalyst of choice.

We wish to report now that acetals and ketals are reductively cleaved very efficiently to the corresponding ethers under Nafion-H catalysis with triethylsilane in refluxing dichloromethane solution. Both benzylic as well

† Nafion is a registered trademark of the Du Pont Company.

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