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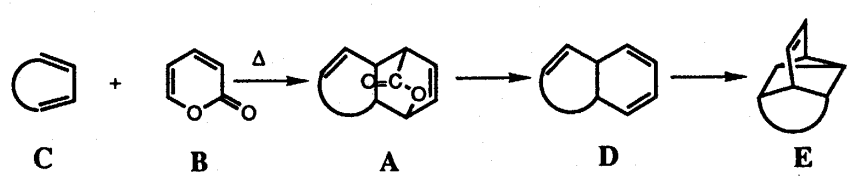
Total Synthesis of Optically-Active Shizuka-acoradienol by Means of High-Pressure Diels-Alder Reaction

Toshihide HATSUI*, Tomokazu HASHIGUCHI and Hitoshi TAKESHITA*

Abstract:—Optically-active shizuka-acoradienol, a spiro[5.4]decadienol metabolite of *Chloranthus japonicus*, was synthesized starting from an inversely-electron-demanded Diels-Alder reaction of (3*R*)-irida-2(7),5-diene with 5-methoxycarbonyl-2-pyrone.

Diels-Alder adducts (**A**) of α-pyrone derivatives (**B**) to conjugated dienes (**C**) form cyclohexadienes (**D**), upon spontaneous cheletropic removel of carbon dioxide, further proceeded intramolecular Diels-Alder reaction with the mode of the inverse electron demand to form tricyclo[3.2.1.$0^{2,6}$]octene derivative (**E**).[1)]



(Schgeme 1)

Recently, we have completed a total synthesis a *cis*-decaline sesquiterpenoid, 10-epi-juneol, by employing only the first step of this inversely-electron-demanded Diels-Alder reaction with α-terpinene.[2)] At the same time, it is obvious that in a case of *transoid*-dienes, the second intramolecular step of the reaction can not occur. This procedure can be, therefore, applied to construct spirocyclic compounds from methylenecycloalkenes.

Herein, we describe a facile synthesis of shizuka-acoradienol (**1**),[3)] a metabolite of *Chloranthus japonicus*,[4)] from the Diels-Alder adduct obtained form (3*R*)-irida-2(7),5-diene (**2**), which can be derived from the photocycloadduct of methyl 2,4-dioxopentanoate to isoprene,[5,6)] and methyl coumalate (5-methoxycarbonyl-2-pyrone, **3**). The following retrosynthetic scheme of **1** from **2** and **3** shows appropriate arrangement of the functional groups.

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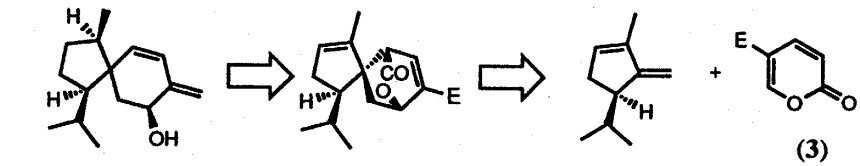
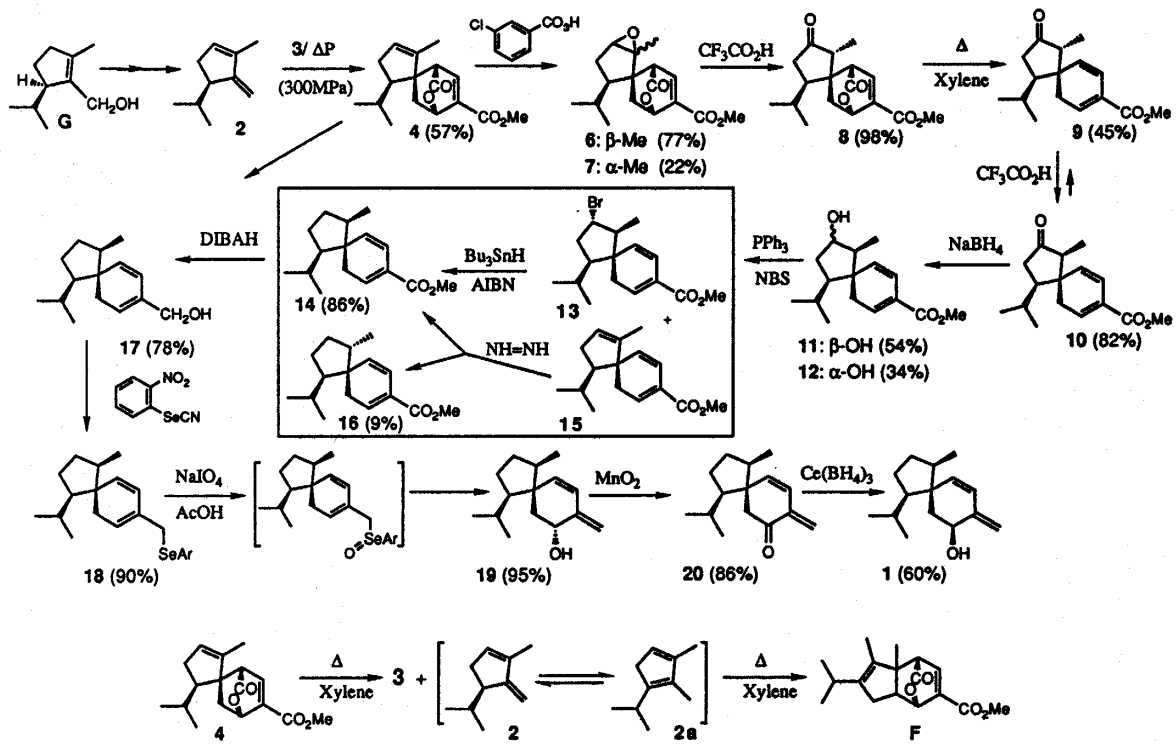


Shizuka-acoradienol (1) **(3*R*)-Irida-2(7),5-diene (2)**

(Scheme 2)

When **2** and **3** were heated at 50 °C under 300 MPa in chloroform, a 1:1-Diels-Alder adduct (**4**) was formed in 57% yield. No decarboxylated product was detected. Refluxing an *o*-xylene solution of **4** caused *retro*-Diels-Alder process to regenerate **3**, which eventually led to accumulate the thermodynamically-controlled Diels-Alder adduct (**F**) with 1-isopropyl-2,3-dimethylcyclopentadiene (**2a**), an isomer of **2**.

A dihydro derivative of **2**, (3*R*)-irid-2(7)-ene (**5**), was unreactive with **3** under those conditions to recover the starting materials.



(Scheme 3)

To prevent the *retro*-Diels-Alder process, **4** was oxidized with *m*-chloroperbenzoic acid to afford qantitatively an epimeric mixture of monoepoxides (**6** and **7**). Prior to thermolysis, a mixture of **6** and **7** was treated with trifluoroacetic acid to give a cyclopentanone (**8**) with retained spirocyclic lactone system in 98% yield. Refluxing an *o*-xylene solution of **8** gave a mixture of decarboxylated spirocyclohexadienes (**9**) and its epimer **10**, in 45% yield. Treatment of **9** with trifluoroacetic acid facilitated the isomerization to **10** (**9**:**10**=1:5).

The oxygen functions of **9** and **10** were removed as follows: the 1:5-mixture of **9** and **10** was reduced with sodium borohydride to give an alcohol (**11**) and its isomer (**12**) in 52 and 34% yields, respectively. This mixture was successively treated with *N*-bromosuccinimide and triphenylphosphine[8] and with tributyltin hydride and a radical initiator, AIBN, to form, via a bromo derivative (**13**), a deoxygenation product (**14**) and dehydration product (**15**). Again, the mixture of **15** and **14** was subjected to the diimide reduction.[9] The colorless oily products thus obtained was constituted of the desired **14** and its epimer (**16**) in 86 and 9% yields, respectively.[10]

Then, **14** was reduced with diisobutylaluminum hydride at -78 °C to give a primary alcohol (**17**) in 78% yield. Allylic rearrangement of the alcohol function by means of Grieco's method[11] proceeded smoothly; treatment of **17** with *o*-nitrophenylselenocyanide and tributylphosphine afforded a phenylseleno derivative (**18**), which was oxidized with sodium metaiodate and acetic acid in aqueous tetrahydrofuran to give **19** in 95% yield. The **19** was not identical with natural product, but its epimer. Manganese(IV) oxide-oxidation of **19** afforded a methylene-ketone derivative (**20**) and its reduction with sodium borohydride and added cerium(III) chloride gave a 3:2-mixture of **1** and **19** in a quantitative yield. This completed a total synthesis of a spirocyclic sesquiterpenoid, **1**, via a high-pressure Diels-Alder reaction.

Experimental

The elemental analyses were carried out by Mrs. Y. Hatazoe of the Institute of Advanced Material Study, Kyushu University. The melting points were measured with a Yanagimoto Micro Melting Point apparatus and are uncorrected. The NMR spectra were measured by means of JEOL FX 100 Model and GSX 270H Model spectrometers in $CDCl_3$; the chemical shifts are expressed in δ units. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily compounds, using a JASCO IR-A102 spectrometer. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane. Some of the new compounds lack elemental analyses due to a long-term out-of-order of the facility, but they were reasonably characterized by other means.

Preparation of 2. A collidine solution (36 cm^3) of (3*R*)-1-iriden-7-ol (**G**, 10.42 g) prepared from a photocycloadduct of methyl 2,4-dioxopentanoate to isoprene,[5] was added dropwise to an anhydrous benzene solution (200 cm^3) of $MeSO_2Cl$ (9.3 g) in 1-h period, and the mixture was stirred another 15 h at room temperature. The mixture was then extracted with EtOAc, and chromatographed on a silica-gel column to give **2** [a colorless oil, 5.50 g, 57%. ^1H NMR δ=0.70 (3H, d, J=7.0 Hz), 0.72 (3H, d, J=7.0 Hz), 1.74 (3H, td, J=3.7, 2.2 Hz), 1.91 (1H, spet d, J=7.0, 4.2 Hz), 2.16 (1H, dm, J=17.3 Hz), 2.30 (1H, ddm, J=17.3, 7.6 Hz), 2.75 (1H, ddm, J=7.6, 7.2 Hz), 4.82 (1H, d, J=2.0 Hz), 4.84 (1H, d, J=2.0 Hz), and 5.70 (1H, br s). ^{13}C NMR δ=12.5, 16.0, 20.5, 31.7, 47.5, 100.2, 134.1, 140.7, and 158.6. IR ν: 2940, 1616, 1465, 1384, 1366, 1022, 857, and 733 cm^{-1}].

High-Prssure Diels-Alder Reaction of 2 and 3. Formation of 4. A $CHCl_3$ solution of **2** (651 mg) and **3** (370 mg) was heated at 50 °C under 300 MPa. The mixture was then chromatographed on a silica-gel column to give **4** [colorless neddles, mp 149.6-149.9 °C, 397 mg, 57%. $[\alpha]_D^{25}=-52.6°$ ($CHCl_3$, c=0.74). Found: C, 70.01; H, 7.59%. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64%. ^1H MNR δ=0.49 (3H, d, J=7.0 Hz), 0.83 (3H, d, J=7.0 Hz), 1.68 (3H, td, J=2.9, 1.5 Hz), 1.60 (1H, m), 1.83 (1H, dd, J=7.0, 3.3 Hz), 1.95 (1H, dd, J=15.0, 1.5 Hz), 2.09 (1H, dt, J=17.2, 1.5 Hz), 2.35 (1H, dd, J=15.0, 4.0 Hz), 2.41 (1H, m), 3.44 (1H, d, J=6.6 Hz), 3.83 (3H, s), 5.55 (1H, dq, J=3.3, 1.5 Hz), 5.74 (1H, m), and 7.32 (1H, dd, J=6.6, 2.2 Hz). ^{13}C NMR δ= 13.8, 17.3, 21.1, 28.5, 29.1, 52.2, 52.8, 53.1, 55.2, 74.2, 128.4, 136.8, 141.8, 142.5, 162.8, and 172.1. IR ν: 2970, 1768, 1720, 1633, 1464, 1437, 1305, 1257, 1161, 1096, and 1008 cm^{-1}. MS m/z, 290 (M^+, 0.1), 154 (6), 137 (7), 136 (63), 95 (8), and 94 (100)].

Attempted High-Presure Diels-Alder Reaction of 3 and 5. A $CHCl_3$ solution of **3** (158 mg) **5** (216 mg) was heated at 100 °C under 300 MPa. After being heated at 100 °C for 10 h, the starting materials were recovered unchanged.

MCPBA-Oxdation of 4 to 6 and 7. A CH_2Cl_2 solution (10 cm^3) of **4** (251 mg) was oxidized with MCPBA (218 mg) at room temperature for 15 h. The mixture was then washed with aq $NaHCO_3$ and extracted with ether. Silica-gel column chromatography of the mixture afforded **6** [colorless needles, mp 163.9-165.2 °C, 205 mg, 77%. $[\alpha]_D^{25}=+30.0°$ ($CHCl_3$, c=0.41). Found: C, 66.71; H, 7.27%. Calcd for $C_{18}H_{22}O_5$: C, 66.65; H, 7.24%. ^1H MNR δ=0.73 (3H, d, J=6.6 Hz), 0.86 (3H, d, J=6.6 Hz), 1.43 (1H, br m), 1.44 (1H, br m), 1.54 (1H, ddd, J=13.6, 10.3, 1.5 Hz), 1.71 (1H, ddd, J=10.3, 7.4, 1.5 Hz), 1.85 (1H, dd, J=14.3, 1.8 Hz), 1.93 (1H, dd, J=13.6, 7.4 Hz), 2.28 (1H, dd, J=14.3, 4.0 Hz), 3.29 (1H, br s), 3.72 (1H, dd, J=6.6 Hz), 3.83 (3H, s), 5.75 (1H, m), and 7.35 (1H, dd, J=6.6, 2.7 Hz). ^{13}C NMR δ=15.1, 19.1, 24.7, 26.4, 27.1, 29.6, 47.5, 50.3, 50.5, 52.3, 64.6, 67.0, 73.9, 137.7, 140.2, 162.3, and 171.7. IR ν: 2970, 1773, 1722, 1439, 1294, 1259, 1158, 1095, 1002, 941, and 917 cm^{-1}. MS m/z, 306 (M^+, 21), 263 (77), 152 (62), 137 (100), 110 (84), 109 (73), and 43 (48).] and **7** [colorless needles, mp 170.6-171.8 °C, 58 mg, 22%. $[\alpha]_D^{25}=+7.8°$ ($CHCl_3$, c=0.15). Found: C, 66.47; H, 7.19%.

^{1}H MNR δ=0.71 (3H, d, J=6.6 Hz), 0.72 (3H, d, J=6.6 Hz), 1.32 (1H, sept d, J=6.6, 3.6 Hz), 1.41 (3H, s), 1.62 (1H, dt, J=9.6, 3.6 Hz), 1.90 (1H, dd, J=15.0, 3.6 Hz), 2.10 (1H, dd, J=15.0, 1.8 Hz), 1.96 (1H, dd, J=15.0, 3.6 Hz), 2.10 (1H, dd, J=15.0, 1.8 Hz), 2.43 (1H, dd, J=15.0, 3.3 Hz), 3.32 (1H, s), 3.53 (1H, d, J=6.6 Hz), 3.83 (3H, s), 5.73 (1H, dt, J=3.3, 1.8 Hz), and 7.31 (1H, dd, J=6.6, 2.2 Hz). ^{13}C NMR δ=14.6, 18.0, 23.9, 26.2, 29.7, 30.9, 50.5, 50.8, 51.6, 52.3, 63.0, 68.4, 74.1, 138.0, 141.3, 162.8, and 172.3. MS m/z, 306 (M^+, 2), 264 (16), 263 (100), 155 (30), 137 (41), 110 (33), 109 (64), and 43 (21). IR ν: 2970, 1767, 1722, 1436, 1275, 1245, 1158, 1093, 1037, and 998 cm^{-1}].

Trifluoroacetic Acid Treatment of 6 to 8. A CF_3CO_2H solution (5 cm^3) of **6** (112 mg) was stirred at room temperature for 15 min. The mixture was then evaporated in vacuo, and the residue thus obtained was chromatographed on a silica-gel column to give 8 [a colorless oil, 110 mg, 98%. $[\alpha]_D^{25}$=+63.2° (c=0.69, $CHCl_3$). ^{1}H NMR δ=0.77 (3H, d, J=7.0 Hz), 0.92 (3H, d, J=7.0 Hz), 1.17 (3H, d, J=7.0 Hz), 1.78 (1H, sept d, J=7.0, 3.7 Hz), 2.03-2.16 (2H, m), 2.22-2.39 (4H, m), 3.50 (1H, d, J=6.6 Hz), 3.84 (3H, s), 5.72 (1H, dt, J=4.0, 2.2 Hz), and 7.40 (1H, dd, J=6.6, 2.2 Hz). ^{13}C NMR δ=9.9, 18.0, 23.7, 27.8, 34.3, 36.5, 47.0, 48.2, 49.0, 52.4, 56.0, 73.8, 137.3, 141.2, 162.4, 171.3, and 216.4. MS m/z, 306 (M^+, 4), 249 (6), 219 (39), 191 (22), 187 (22), 164 (69), 110 (48), 105 (100), 91 (19), 81 (27), 69 (29), and 54 (34). IR ν: 2960, 1755, 1718, 1441, 1381, 1307, 1254, 1096, 1023, 916, and 753 cm^{-1}].

Thermolytic Decarboxylation of 8 to 9. An *o*-xylene solution of 8 (378 mg) was refluxed for 2 h. The mixture was then chromatographed on a silica-gel column to give **9** [a colorless oil, 146 mg, 45%. $[\alpha]_D^{25}$=+266° (c=0.32, $CHCl_3$). ^{1}H NMR δ=0.95 (3H, d, J=6.6 Hz), 0.95 (3H, d, J=7.7 Hz), 1.03 (3H, d, J=6.6 Hz), 1.72 (1H, m), 1.93-2.05 (2H, m), 2.08 (1H, dd, J=18.2, 5.0 Hz), 2.46 (1H, m), 2.55 (1H, q, J=6.6 Hz), 2.67 (1H, dd, J=18.2, 3.3 Hz), 3.77 (3H, s), 5.67 (1H, d, J=10.3 Hz), 6.38 (1H, dd, J=10.3, 1.1 Hz), and 6.87 (1H, br s). ^{13}C NMR δ=11.8, 22.2, 22.4, 29.9, 30.0, 40.6, 43.7, 49.5, 50.7, 51.8, 120.7, 128.9, 135.2 (2C), 165.7, and 220.4. IR ν: 2970, 2885, 1726, 1438, 1340, 1257, 1199, 1097, 1076, 948, and 728 cm^{-1}] and **10** (140 mg, 44%).

Trifluroacetic Acid-Induced Isomerization of 9 to 10. A CF_3CO_2H solution (5 cm^3) of **9** (146 mg) was heated at 50 °C for 15 h. The mixture was then heated in vacuo, and the residue thus obtained was chromatographed on a silica-gel column to give a mixture (120 mg, 82%) of **9** and **10** [a colorless oil. ^{1}H NMR δ=0.93 (3H, d, J=6.6 Hz), 0.96 (3H, d, J=6.2 Hz), 1.04 (3H, d, J=6.2 Hz), 1.62-1.88 (3H, m), 1.96 (1H, dd, J=20.2, 6.2 Hz), 2.04 (1H, q, J=6.2 Hz), 2.50 (1H, m), 2.63 (1H, dd, J=20.2, 3.3 Hz), 3.76 (3H, s), 5.56 (1H, d, J=9.9 Hz), 6.37 (1H, dd, J=9.9, 1.5 Hz), and 6.82 (1H, m). ^{13}C NMR δ=8.1, 22.0, 22.6, 24.9, 30.2, 41.2, 45.1, 51.8, 53.1, 59.4, 120.0, 127.3, 135.2 (2C), 165.8, and 217.3. IR ν: 2965, 2870, 1746, 1723, 1434, 1340, 1159, 1098, 1073, 1045, 941, and 892 cm^{-1}] with an improved ratio (1:5).

Reduction of 9 and 10 to 11 and 12. An MeOH solution (3 cm^3) of **9** and **10** (1:5, 95 mg) was reduced with $NaBH_4$ (20 mg) at 0 °C for 30 min. The mixture was then treated with

acetone and extracted with EtOAc. The organic extract was then heated in vacuo to remove the solvent, and the residue was chromatographed on a silica-gel column to give an inseparable mixture (a coloress oil, 83 mg, 89%) of **11** [^{1}H NMR δ=0.91 (3H, d, J=6.6 Hz), 0.94 (3H, d, J=7.3 Hz), 0.96 (3H, d, J=6.6 Hz), 1.21-1.40 (2H, m), 1.44 (1H, quint, J=7.1 Hz), 1.65 (1H, d sept, J=9.5, 6.6 Hz), 2.38-2.56 (2H, m), 2.72 (1H, dm, J=5.9 Hz), 3.75 (3H, s), 4.14 (1H, td, J=6.6, 3.7 Hz), 5.29 (1H, d, J=9.9 Hz), 6.27 (1H, dd, J=9.9, 1.5 Hz), and 6.88 (1H, t, J=4.8 Hz). ^{13}C NMR δ=8.7, 22.3, 22.4, 25.0, 30.1, 39.9, 45.9, 51.5, 51.8, 57.9, 73.7, 119.2, 126.7, 137.2, 137.6, and 166.3. MS m/z, 264 (M^+, 3), 246 (2), 203 (24), 191 (87), 176 (34), 164 (92), 163 (68), 149 (82), 131 (61), 105 (100), 91 (60), 77 (17), and 57 (29). IR ν: 3510, 2965, 1705, 1438, 1258, 1082, 964, 722, and 694 cm^{-1}] and its epimers **12**, in a ratio of 5:3.

Deoxygenation Reaction of 11 and 12. Formation of 14 and 16. A mixture of **11** and **12** (318 mg) dissolved in THF (10 cm^3) was treated with NBS (321 mg) and PPh_3 (473 mg) at room temperature for 1 h. The mixture was then chromatographed on a silica-gel column to obtain a colorless oily mixture (334 mg, 3:2), which was dissolved in toluene (5 cm^3) and was treated with AIBN (96 mg) and Bu_3SnH (582 mg) at 60 °C for 10 min to give **14** and a presence of dehydrated olefin, **15**. The mixture was, without isolation, further treated with diimide[9] to finally give a 9:1-mixture (a coloress oil, 164 mg, 95%) of **14** [^{1}H NMR δ=0.81 (3H, d, J=6.6 Hz), 0.88 (3H, d, J=6.6 Hz), 0.94 (3H, d, J=6.6 Hz), 1.13-1.90 (7H, m), 2.13 (1H, dd, J=20.5, 5.9 Hz), 2.41 (1H, dd, J=20.5, 3.3 Hz), 3.75 (3H, s), 5.38 (1H, J=9.9 Hz), 6.25 (1H, dd, J=9.9, 1.1 Hz), and 6.84 (1H, m). ^{13}C NMR δ=14.5, 22.2, 22.6, 23.6, 28.0, 28.1, 30.5, 46.5, 46.8, 51.5, 59.2, 118.9, 127.1, 136.6, 137.8, and 166.8. IR ν: 2950, 1725, 1440, 1255, and 1075 cm^{-1}] and its epimers **16**.

Reduction of 14 with DIBAH to 17. A toluence solution of **14** containing **16** (515 mg) was treated with DIBAH (10 cm^3, 0.93 M in hexane) at −78 °C to give **17** [a coloress oil, 410 mg, 89%. ^{1}H NMR δ=0.84 (3H, d, J=6.6 Hz), 0.87 (3H, d, J=6.6 Hz), 0.96 (3H, d, J=6.6 Hz), 1.12-1.86 (7H, m), 1.96 (1H, dd, J=18.7, 5.5 Hz), 2.28 (1H, dd, J=18.7, 1.8 Hz), 4.02 (2H, br s), 5.34 (1H, d, J=9.9 Hz), 5.55 (1H, br s), and 5.91 (1H, dd, J=9.9, 1.4 Hz). ^{13}C NMR δ=14.6, 22.3, 22.5, 28.0 (2C), 30.5, 46.7, 46.9, 59.4, 65.6, 121.2, 121.4, 133.6, and 138.1. MS m/z, 220 (M^+, 23), 147 (21), 135 (100), 107 (20), 105 (35), 91 (52), 79 (22), and 41 (25). IR ν: 3340, 2965, 2890, 1462, 1377, 1041, 1007, and 825 cm^{-1}].

Allylic Rearrangement of Alcoholic Function of 17 to 19 by Means of Grieco's Method. A CH_2Cl_2 solution (3 cm^3) of **17** (56 mg) was treated with o-$NO_2C_6H_4SeCN$ (116 mg) and PBu_3 (103 mg) at 0 °C for 1 h. The mixture was then chromatographed on a Florisil column to give an aryselenyl derivative (**18**) [a coloress oil, 92 mg, 90%. ^{1}H NMR δ=0.74 (3H, d, J=6.6 Hz), 0.86 (3H, d, J=6.6 Hz), 0.94 (3H, d, J=6.6 Hz), 1.10-1.85 (7H, m), 1.94 (1H, dd, J=19.4, 5.5 Hz), 2.27 (1H, dm, J=19.4 Hz), 3.53 (1H, d, J=11.4 Hz), 3.63 (1H, d, J=11.4 Hz), 5.34 (1H, d, J=9.5 Hz), 5.65 (1H, br s), 5.81 (3H, dd, J=9.5, 1.4 Hz), 7.25-7.32 (1H, m), 7.47-7.56 (2H, m), and

8.25 (1H, dd, J=8.0, 1.5 Hz). ^{13}C NMR δ=14.6, 22.3, 22.6, 23.0, 28.1 (2C), 30.5, 32.1, 46.4, 46.7, 59.4, 122.9, 124.1, 125.3, 126.2, 128.0, 129.7, 133.3, 134.3, 138.6, and 147.9. IR ν: 2960, 2875, 1588, 1507, 1315, 1302, 1097, 1038, 943, 854, 782, and 729 cm^{-1}]. Subsequently, **18** (48 mg) was oxidized with $NaIO_4$ (166 mg) and AcOH in aqueous THF (3%, 4 cm^3) at room temperature for 15 h to give **19** [colorless neddles, mp 101.7-102.9 °C, 32 mg, 95%. $[\alpha]_D^{25}$=+243° (c=0.23, $CHCl_3$). ^{1}H MNR δ=0.82 (3H, d, J=6.6 Hz), 0.84 (3H, d, J=6.6 Hz), 0.91 (3H, d, J=6.6 Hz), 1.22-1.53 (5H, m), 1.67-1.91 (5H, m), 4.53 (1H, m), 4.92 (1H, br s), 5.18 (1H, br s), 5.33 (1H, d, J= 9.9 Hz), and 6.10 (1H, d, J=9.9 Hz). ^{13}C NMR δ=15.9, 21.8, 22.9, 28.2, 29.7, 30.8, 32.1, 45.7, 50.5, 59.3, 67.5, 107.8, 126.6, 140.3, and 146.4. MS m/z, 220 (M^+, 3), 202 (47), 159 (86), 136 (54), 132 (55), 131 (35), 120 (38), 119 (32), 118 (100), 91 (53), 69 (64), 55 (36), and 41 (40). IR ν: 3630, 2975, 2895, 1463, 1370, 1092, 1032, 1009, and 891 cm^{-1}].

Oxidation of 19 to 20. A mixture of **19** (26.4 mg) and MnO_2 (235 mg) in CH_2Cl_2 solution (2 cm^3) was refluxed for 2 h to obtain **20** [acolorless oil, 22.7 mg, 86%. ^{1}H NMR δ=0.71 (3H, d, J=6.6 Hz), 0.89 (3H, d, J=6.6 Hz), 0.91 (3H, d, J=6,2 Hz), 1.25-1.90 (7H, m), 2.34 (1H, d, J= 16.5 Hz), 2.43 (1H, d, J=16.5 Hz), 5.16 (1H, br s), 5.71 (1H, d, J=9.9 Hz), 5.94 (1H, t, J=1.5, and 6.40 (1H, d, J=9.9 Hz). ^{13}C NMR δ=14.0, 22.1, 22.7, 28.1, 29.4, 30.9, 39.6, 45.9, 52.5, 58.6, 118.3, 126.1, 138.9, 140.8, and 200.4. IR ν: 2985, 2900, 1712, 1467, 1372, 1317, 1167, 1137, and 928 cm^{-1}].

Reduction of 20 with $Ce(BH_4)_3$ to 1 and 19. An MeOH solution (1 cm^3) of **20** (5.6 mg) was reduced with $NaBH_4$ (5.1 mg) and $CeCl_3$ (51 mg) at 0 °C to give 1[colorless needles, mp 126.3-127.4 °C, 3.3 mg, 60%. $[\alpha]_D^{25}$=−204° (c=0.090, $CHCl_3$) (lit.[4]) mp 128.5-130.0 °C, $[\alpha]_D^{25}$= −203°). ^{1}H NMR δ=0.74 (3H, d, J=6.6 Hz), 0.86 (3H, d, J=6.6 Hz), 0.90 (3H, d, J=6.2 Hz), 1.11 (1H, m), 1.27 (1H, t, J=12.2 Hz), 1.44 (2H, m), 1.6-1.9 (6H, m), 4.48 (1H, m), 4.93 (1H, br s), 5.19 (1H, br d, J=1.4 Hz), 5.32 (1H, d, J=9.9 Hz), and 6.15 (1H, d, J=9.9 Hz). ^{13}C NMR δ= 13.7, 22.9, 23.4, 27.3, 29.2, 30.4, 31,4, 47.2, 50.8, 57.8, 67.7, 109.7, 127.3, 140.1, and 146.7] and **19** (2.3 mg, 40%).

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和文概要

5-メトキシカーボニル-α-ピロンと光学活性 (3*R*)-イリダ-2(7),5-ジェンの高圧環状加反応によってシズカアコラジェノールを全合成した。