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Rearrangement Approaches to Polycyclic Skeletons. 2. Synthesis of the Gibberellin Skeleton[1]

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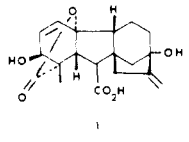
Received September 6, 1978

The intriguing and challenging synthetic objectives presented by the gibberellins,[2] represented in their full structural complexity by gibberillic acid, GA_3 (**1**), have received considerable attention. These efforts include model studies directed toward preparation of the sensitive array of functionality in ring A[3] as well as the total syntheses of gibberellins GA_4[4a] and GA_{15}.[4b] We now wish to describe an efficient, convergent method to prepare the tetracyclic carbon skeleton characteristic of gibberellins such as GA_9 (**2**).[2] The overall



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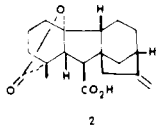
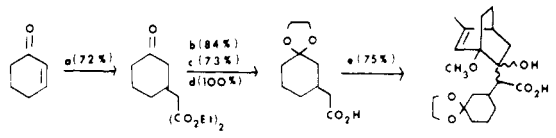


2

synthetic strategy employed in this work involves initial formation of a bridgehead-substituted bicyclo[3.2.1]octenone derivative followed by elaboration of the fused-ring framework.[1b]

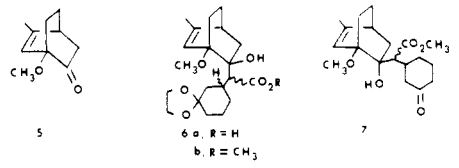
The A/B ring precursor, ketal acid **3**, was prepared from 2-cyclohexenone as shown in Scheme I. Conversion of ketal acid **3** into its lithium dianion by sequential treatment with lithium hydride and lithium diisopropylamide, followed by addition of the C/D ring precursor, the Diels–Alder derived 1-methoxy-5-methylbicyclo[2.2.2]oct-5-en-2-one (**5**),[1b] furnished a mixture of epimeric β-hydroxy acids **4** in 75% yield. This reaction mixture was crystallized to furnish pure exo alcohol acid **6a** in 27% yield. Aqueous acid hydrolysis of the resulting mother liquors, followed by esterification with diazomethane, yielded the crystalline endo alcohol ester **7** in 20% yield. Based on the expected shielding effect[1b] of the C_5–C_6

Scheme I



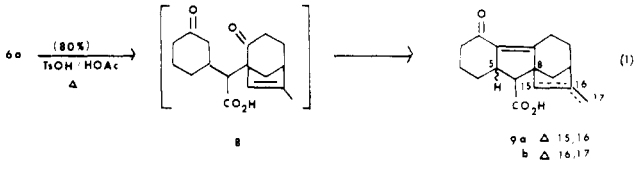
[a] Diethyl malonate, EtONa, EtOH, −5 to 25 °C, 6 h. [b] Ethylene glycol, TsOH, benzene, Δ, 12 h. [c] NaCN, Me_2SO, 155 °C, 16 h. [d] KOH, H_2O, 100 °C, 2 h. [e] (i) LiH, THF; (ii) LDA, THF, −40 to 40 °C; (iii) addition of ketone **5**, 0 to 25 °C, 12 h.

double bond of the bicyclo[3.2.1]octene nucleus, the exo/endo stereochemical assignments for these products were made by comparing the chemical shifts of the methyl esters, δ 3.67 for the exo alcohol ester **6b** and δ 3.73 for the endo alcohol ester **7**. The relative stereochemistry of the remaining chiral centers in **6** and **7** has not been assigned.



5 **6a**, R = H; **b**, R = CH_3 **7**

Treatment of exo alcohol acid **6a** with a catalytic amount of *p*-toluenesulfonic acid in acetic acid furnished a nonseparable mixture (4:1) of crystalline acid products in 80% yield (eq 1). The major product was assigned the tetracyclic structure **9a** on the basis of spectra data while the minor isomer was identified as the exocyclic methylene isomer **9b** (see Experimental Section for details). The formation of these products is consistent with the intermediacy of the expected[1b] 1-substituted bicyclo[3.2.1]oct-6-en-2-one **8** followed by acid-catalyzed Aldol cyclization and, in the case of **9b**, concomitant

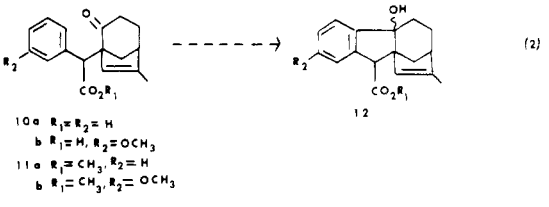


(1)

8 **9a** Δ 15,16; **b** Δ 16,17

isomerization of the isolated double bond. Although the relative stereochemistry of the C-5 and C-8 centers in **9a** has not been assigned, a single isomer appears to have been formed which, in turn, suggests that the starting exo alcohol acid **6a** is a single diastereomer. Since both the A/B and C/D ring precursor units can be readily modified to incorporate a variety of functionalities, this convergent route involving closure of the B ring via an Aldol cyclization constitutes a promising method to prepare a number of naturally occurring gibberellins.

A second synthetic approach to the tetracyclic gibberellin skeleton was also evaluated. As shown in eq 2 this sequence



(2)

10a $R_1 = R_2 = H$; **b** $R_1 = H$, $R_2 = OCH_3$
11a $R_1 = CH_3$, $R_2 = H$; **b** $R_1 = CH_3$, $R_2 = OCH_3$ **12**

involved attempted formation of the five-membered B ring by intramolecular electrophilic cyclization[5] of the 1-aryl-substituted bicyclo[3.2.1]octenones **10** and **11** to give the aromatic A ring gibberellin derivatives **12**.

Treatment of keto acid **10a**[1b] with *p*-toluenesulfonic acid (0.5 equiv) in benzene at reflux for 6 h yielded a single product in 71% yield which was assigned as the α,β-unsaturated δ-lactone **13** on the basis of spectral data (see Experimental

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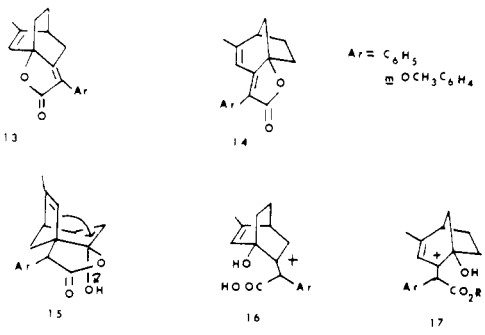
Section). Although exposure of keto ester **11a** to *p*-toluenesulfonic acid (0.5 equiv) in benzene (Δ, 6 h) and to $AlCl_3$ (CH_2Cl_2, 25 °C, 24 h) resulted in recovery of starting material, reaction of ester **11a** with poly(phosphoric acid) (80 °C, 2 h) gave an isomeric lactone **14** as the only observed product in 82% yield. The extended conjugation of the lactone moiety of **14** (308 nm, ε 18 000 vs 262 nm, ε 11 000 for lactone **13**) requires the presence of a bicyclo[3.2.1]octane carbon skeleton, and together with the other spectra data shown in the Experimental Section establish the structure assignment for this rearrangement product. Parallel results were observed for the *m*-methoxyaryl acid **10b** and ester **11b.** In addition, treatment of keto acid **10b** with poly(phosphoric acid) (80 °C, 2 h) yielded the bicyclo[3.2.1]octenyl lactone **14** as the only observed product in 92% yield.

The relative ease with which the keto acids **10** undergo rearrangement in the presence of *p*-toluenesulfonic acid (the corresponding esters **11** do not rearrange under these conditions) and the regioselectivity observed in the rearrangement of these substrates are consistent with the initial formation of lactol **15** followed by net migration of the anti-disposed unsaturated two-carbon bridge to give the nonconjugated cation **16** which yields the bicyclo[2.2.2]octenyl lactone **13.** In contrast to this apparent kinetic control pathway, treatment of both keto acids **10** and keto esters **11** with poly(phosphoric acid) results in skeletal rearrangement to give the thermodynamically more stable allylic cation **17** (or its enol analogue)



which then yields the fully conjugated bicyclo [3.2.1]octenyl lactone **14.** Apparently the presence of the C_6–C_7 double bond in these 1-aryl-substituted bicyclo[3.2.1]octenones **10** and **11** effectively precludes the intramolecular cyclization pathway outlined in eq 2 to give the gibberellin skeleton.

Experimental Section

General. All reactions were carried out in an inert nitrogen atmosphere and were routinely monitored by TLC. Melting points were determined on a Mel-temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237B grading infrared spectrometer; ^{1}H-NMR spectra were measured on a Perkin-Elmer R-12 spectrometer, a Varian A-60 instrument equipped with cross-correlation, or a Varian HA-100 instrument and chemical shifts are reported in ppm downfield (δ) from internal Me_4Si. ^{13}C-NMR spectra were obtained on a Bruker WH90 instrument and chemical shifts are reported in ppm downfield (δ) from internal Me_4Si. High resolution mass spectra were obtained using a CEC Model 21-100 mass spectrometer. The microanalytical determination was done by Chemalytics, Inc., Tempe, Ariz.

Cyclohexanone-3-acetic Acid Ketal 3. Diethyl cyclohexanone-3-malonate (66.0 g, 0.26 mol), prepared from 2-cyclohexenone in 72% isolated yield using the procedure of Bartlett,[6] ethylene glycol (16.1 g, 0.26 mol), and TsOH (0.3 g) in benzene (40 mL) were heated at reflux for 12 h with continuous separation of water using a Dean-Stark apparatus. The cooled mixture was washed with aqueous $NaHCO_3$ solution and then water. After drying and removal of the solvent at reduced pressure, the residue was distilled to yield 66.0 g (84%) of diethyl cyclohexanon-3-malonate ketal: bp 150–165 °C (0.3 mm); IR (CCl_4) 1730 cm^{-1}; NMR (CCl_4) δ 1.26 (t, 6, J = 7 Hz), 1.40–2.60 (m, 9), 3.10 (d, 1, J = 8 Hz), 3.85 (s, 4), and 4.13 (q, 4, J = 7 Hz). Treatment of ketal malonate (53.6 g, 0.18 mol) with sodium cyanide (26.2 g, 0.54 mol) in Me_2SO (320 mL)[7] at 155 °C for 16 h, followed by distillation to reduce the volume to ca. 100 mL, addition of water (500 mL), and extraction with pentane, furnished, after removal of solvent, a residue which was distilled to give 29.4 g (73%) of ethyl cyclohexanone-3-acetate ketal: bp 110–120 °C (0.3 mm); IR (CCl_4) 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (t, 3, J = 7 Hz), 1.45–2.35 (M, 11), 3.93 (s, 4), and 4.14 (q, 2, J = 7 Hz). Exposure of ketal acetate (29.3 g, 0.13 mol) to KOH (16.9 g, 0.26 mol) in water (50 mL) at 100 °C for 2 h, followed by careful acidification to pH ~4 with dilute hydrochloric acid, yielded 25.5 g (100%) of cyclohexanone-3-acetic acid ketal (**3**) as a viscous liquid: IR ($CHCl_3$) 3300–2800, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.25–2.45 (m, 11), 3.94 (s, 4), and 10.97 (s, 1); mass spectrum, *m/e* (rel intensity) 200 (M^+, 3), 157 (33), 141 (35), 99 (100), and 86 (35).

Anal. ($C_{10}H_{16}O_4$): Calcd mol wt, 200.1048. Found: 200.1053.

***exo*-1-Methoxybicyclo[2.2.2]oct-5-en-2-ol Acid Ketal 6a.** A solution of lithium diisopropylamide, prepared by dropwise addition of *n*-butyllithium in ether (1.4 M, 23 mL, 32 mmol) to diisopropylamine (3.2 g, 32 mmol) at −20 °C, was added to a slurry of the lithium salt of acid ketal **3** (prepared by LiH treatment of **3**, 6.3 g, 31 mmol) in THF (150 mL) at −40 °C. After 30 min, the suspension was warmed to 40 °C for 2 h and cooled to −40 °C and then 1-methoxy-5-methylbicyclo[2.2.2]oct-5-en-2-one (**5**)[1b] (3.98 g, 24 mmol) was added. After being stirred at −40 °C for 2 h, the mixture was allowed to stand 12 h at 25 °C. After addition of ice/water, ether extraction furnished 1.50 g of recovered ketone **3.** Acidification of the aqueous phase with dilute HCl to pH ~3 and ether extraction furnished 4.1 g (75% corrected) of a mixture of acids. Crystallization from ether–hexane yielded 1.5 g (27%) of pure exo acid **6a:** mp 218–219 °C; IR ($CHCl_3$) 3370–2800, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.45 (m, 20), 3.26 (s, 3), 3.94 (s, 4), and 5.86 (m, 1); mass spectrum, *m/e* (rel intensity) 366 (M^+, 1), 141 (12), 125 (37), 124 (100), and 109 (35).

Anal. Calcd for $C_{20}H_{30}O_6$: C, 65.55; H, 8.25. Found: C, 65.75; H, 8.42.

Treatment of acid **6a** with diazomethane gave methyl ester **6b:** mp 150–151 °C; IR ($CHCl_3$) 3550–3350, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.36 (m, 17), 1.77 (d, 3, J = 1.5 Hz), 3.25 (s, 3), 3.67 (s, 3), 3.94 (s, 4), 4.45 (s, 1, –OH), and 5.84 (m, 1).

Anal. Calcd for $C_{21}H_{32}O_6$: C, 66.30; H, 8.48. Found: C, 66.28; H, 8.28.

Treatment of the above mother liquors with aqueous acid and then diazomethane furnished a mixture of keto esters which was crystallized from ether hexane to give 1.1 g (20%) of endo keto acid **7:** mp 164–166 °C; IR ($CHCl_3$) 3570–3375, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.12–2.98 (m, 17), 1.77 (d, 3, J = 1.5 Hz), 3.27 (s, 3), 3.73 (s, 3), 4.08 (s, 1, –OH), and 5.88 (m, 1).

Tetracyclic Gibberellin Skeleton 9a,b. A solution of exo ketal acid **6a** (212 mg, 0.57 mmol) and TsOH (5 mg) in acetic acid (10 mL) was heated at reflux for 4 h. The acetic acid was evaporated at reduced pressure and an ether solution of the residue was extracted with $NaHCO_3$. The basic aqueous phase was acidified with 10% HCl and extracted with ether. After drying, the ether was evaporated and the residue was crystallized from ether–hexane to give 120 mg (80%) of a 4:1 mixture (as judged by NMR) of **9a** and **9b**: mp 151–154 °C; IR ($CHCl_3$) 3550–2800, 1710, 1675, and 1610 cm^{-1}; NMR ($CDCl_3$) δ 1.75 (d), 4.90–5.00 (m, vinyl H's for **9b**), and 5.48 (m, vinyl H for **9a**); mass spectrum, *m/e* (rel intensity) 272 (M^+, 100), 244 (65), 227 (36), and 199 (46).

Treatment of this acid mixture with diazomethane gave a 4:1 mixture of esters **9a,b** (methyl esters), mp 104–106 °C (sublimation and crystallization from pentane), which showed ^{1}H NMR ($CDCl_3$) δ 1.14–3.50 (m), 1.73 (d, J = 2 Hz), 3.73 (s, of **9a**), 3.74 (s, of **9b**), 4.94 (m) and 5.00 (m, both of **9b**), and 5.41 (m, of **9a**); ^{13}C NMR showed olefinic carbon absorptions for the minor isomer at δ 107.17, 129,48, 152.44, and 157.58; the 107 and 157 signals are characteristic of an exo-cyclic methylene group in the gibberellin skeleton.[8]

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.40; H, 7.69.

Bicyclo[2.2.2]octenyl γ-Lactone 13. A mixture of keto acid **10a**[1b] (157 mg, 0.58 mmol), TsOH (52 mg, 0.27 mmol), and benzene (20 mL) was heated at reflux for 6 h with continuous removal of water (Dean-Stark trap). After addition of aqueous $NaHCO_3$, the organic phase was dried and then evaporated to give a residue which was crystallized from ether to yield 100 mg (71%) of pure lactone **13** (Ar = C_6H_5): mp 92–94 °C; IR ($CHCl_3$) 1745 cm^{-1}; NMR ($CDCl_3$) δ 1.45–3.10 (m, 7), 1.85 (d, 3, J = 1.5 Hz), 5.93 (b, 1), and 7.20–7.90 (m, 5); UV (MeOH) max 262 nm (ε = 11 000); mass spectrum, *m/e* (rel intensity) 252 (M^+, 42), 224 (73), 196 (100), 195 (75), 168 (65), 167 (52), 152 (30), and 115 (33).

Anal. ($C_{17}H_{16}O_2$): Calcd mol wt, 252.1150. Found: 252.1156.

Under similar conditions keto acid **10b** (300 mg, 1.0 mmol) yielded 282 mg (92%) of a mixture of γ-lactones **13** and **14** (Ar = *m*-

$OCH_3C_6H_4$) in the ratio of 4:1 as judged by the relative intensities of the signals in the NMR ($CHCl_3$) for the vinyl methyl group and the vinyl proton. **13**, δ 1.87 (d, $J \simeq 2$ Hz) and 5.92 (broad s); **14**, δ 2.03 (d, $J \simeq 2$ Hz) and 6.45 (broad s); for the mixture, IR ($CHCl_3$) 1750 cm^{-1}; NMR ($CHCl_3$) δ 3.82 (s), 7.8–7.4 (m); mass spectrum, *m/e* (rel intensity) 282 (M^+, 100), 254 (60), 226 (70), 198 (35), and 194 (40).

Bicyclo[3.2.1]octenyl γ-Lactone 14. Keto ester **11a** (110 mg, 0.39 mmol), prepared from keto acid **10a** by treatment with diazomethane (100% yield), and poly(phosphoric acid) (12 mL) were stirred for 2 h at 80 °C. The cooled mixture was poured onto ice water and extracted with ether. The combined organic phases were washed with aqueous $NaHCO_3$, dried, and then evaporated to give a residue which was crystallized from ether to yield 98 mg (82%) of pure lactone **14** (Ar = C_6H_5): mp 115–116.5 °C; IR ($CHCl_3$) 1740 and 1645 cm^{-1}; NMR ($CDCl_3$) δ 1.60–2.40 (m, 6), 2.00 (d, 3, J = 1.5 Hz), 2.80 (m, 1), 6.45 (b, 1), and 7.25–7.75 (m, 5); UV (MeOH) max 308 nm (ϵ = 18 000); mass spectrum, *m/e* (rel intensity) 252 (106), 224 (58), 196 (70), and 195 (50).

Anal. ($C_{17}H_{16}O_2$); Calcd mol wt, 252.1150. Found: 252.1153.

Under the conditions described above, both keto acid **10b** and keto ester **11b** furnished γ-lactone **14** (Ar = *m*-$OCH_3C_6H_4$) in yields of 92 and 88%, respectively; the crude product showed IR ($CHCl_3$) 1745 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (d, 3, $J \simeq 2$ Hz), 3.82 (s, 3), 6.45 (m, 1), and 7.8–7.5 (m, 4); UV (CH_3OH) max 300 nm.

Registry No.—**3**, 4722-70-7; **5**, 67316-12-5; **6a**, 69089-24-3; **6b**, 69089-25-4; **7**, 69089-26-5; **9a**, 69102-09-6; **9b**, 69089-27-6; **10a**, 67315-97-3; **10b**, 67315-98-4; **11a**, 69089-28-7; **11b**, 69089-29-8; **13** (Ar = C_6H_5), 69089-30-1; **13** (Ar = *m*-$OCH_3C_6H_4$), 69089-31-2; **14** (Ar = C_6H_5), 69089-32-3; **13** (Ar = *m*-$OCH_3C_6H_4$), 69089-33-4; 2-cyclohexenone, 930-68-7; diethyl cyclohexanone-3-malonate ketal, 7084-90-4; ethyl cyclohexanone-3-acetate ketal, 7076-69-9; diethyl cyclohexannone-3-malonate, 22274-75-5.

References and Notes

(1) (a) Financial support of this research by the Robert A. Welch Foundation is gratefully acknowledged. (b) Part 1: S. A. Monti, S-C. Chem. Y-L. Yang, S-S. Yuan, and O. P. Bourgeois, *J. Org. Chem.*, **43**, 4062 (1978).
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X-ray Structure of the γ-Lactone Formed by Acid Treatment of Dihydroisopimaric Acid[1]

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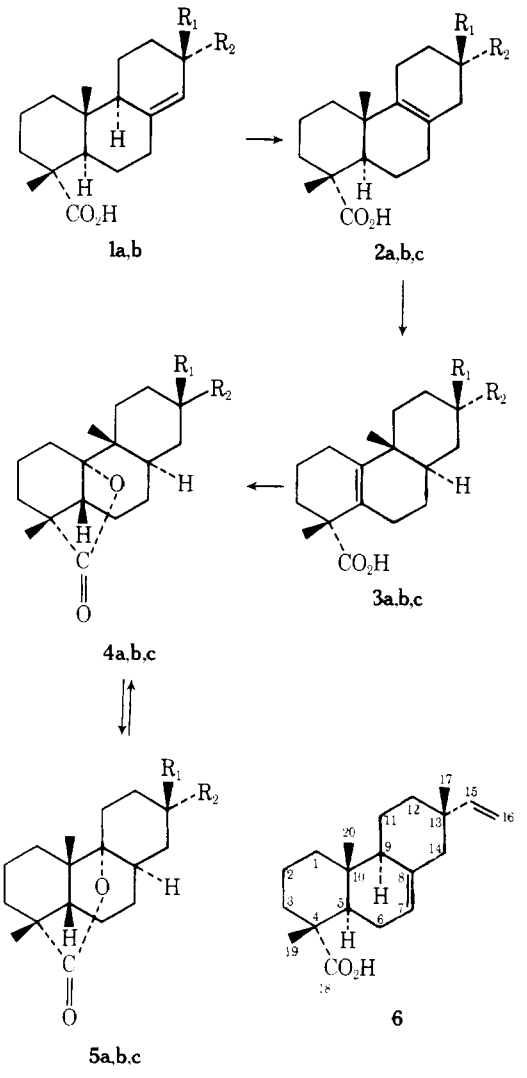
Received October 30, 1978

Exposure of various dihydroabietic and dihydrolevopimaric acids such as **1a** or **2a** to sulfuric acid at low temperature results in formation of a γ-lactone which under somewhat more stringent conditions is in equilibrium with a δ-lactone.[2] The reaction has been formulated in terms of the backbone rearrangement shown in Scheme I, the stereochemistry assigned

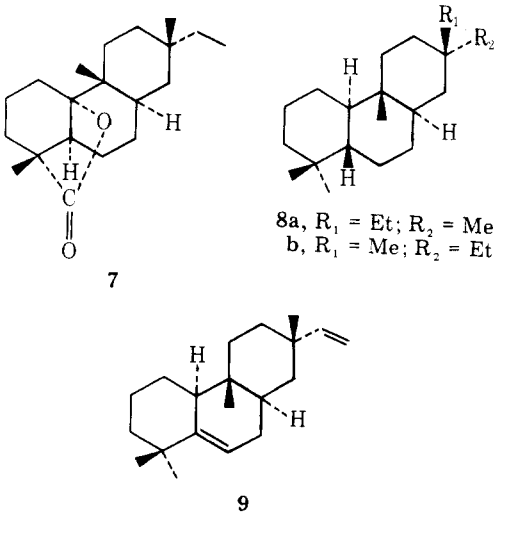
Scheme I[a]



[a] a series, R_1 = isopropyl, R_2 = H; b series, R_1 = Et, R_2 = Me; c series, R_1 = Me, R_2 = Et.

to **4a** and **5a** being based on mechanistic grounds.[3-6] The postulated stereochemistry of **4a** at C-8 and the intermediacy of compounds of type **3** have been verified,[7] but the presumed stereochemistries of **4a** and **5a** at C-5, while extremely plausible, have not been documented independently.

Dihydropimaric acid (**1b**), dihydroisopimaric acid (**6**), and their double-bond isomers likewise undergo rearrangement to γ- and δ-lactones which by analogy have been assigned



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