The 200 g of 3-chloro-3-methyl-2-butanone oxime in 1600 mL of methylene chloride was stirred at 0 °C while nitrosyl fluoride was slowly bubbled into the solution for 1.25 h. The green solution was stirred at 0 °C for 3.5 h, followed by 1.5 h at room temperature. The mixture was slowly poured into saturated aqueous sodium carbonate and washed with saturated aqueous sodium carbonate, water, and brine. The organic layer was dried, filtered, and concentrated in vacuo to give a blue oil which was distilled giving 21.00 g (0.128 mol, 4% overall) of 3-chloro-3-methyl-2-nitriminobutane: bp 48–50 °C/0.5 mm; IR (neat) 6.17, 6.36 (s) and 6.92 μm; NMR ($CDCl_3$) δ 2.24 (s, 3 H, $-(CH_3)C{=}N-$) and 1.83 (s, 6 H, $-((CH_3)_2)CCl$).

Anal. Calcd. for $C_5H_9N_2O_2Cl$: C, 36.49; H, 5.51; N, 17.02; Cl, 21.54. Found: C, 36.30; H, 5.59; N, 17.27; Cl, 21.51.

3-Chloro-3-methyl-2-nitraminobutane (4). Sodium borohydride reduction as above of **3** gave a yellow liquid which was distilled giving a 76% yield of **4** as colorless liquid: bp 60 °C/0.1 mm; IR ($CHCl_3$) 6.35 and 6.88 μm; NMR ($CDCl_3$) δ 8.55 (br m, 1 H, >NH), 4.44 (br q, 1 H, J = 6.5 Hz, $>CH-NHNO_2$), 1.67 (s, 3 H, $>(CH_3)CCl$), 1.64 (s, 3 H, $>(CH_3)CCl$), and 1.39 (d, 3 H, J = 6.5 Hz, $>(CH_3)CNH-$).

Anal. Calcd for $C_5H_{11}N_2O_2Cl$: C, 36.05; H, 6.66; N, 16.81; Cl, 21.28. Found: C, 36.09; H, 6.52; N, 16.28; Cl, 21.49.

1-Oximino-9-chloro-10-methyldecalin and 1-Nitrimino-9-chloro-10-methyldecalin (5). A solution of 58.0 g (0.387 mol) of 10-methyl-$\delta^{1,9}$-octalin[7,8] in 1 L of methylene chloride at 0 °C was stirred while nitrosyl chloride was slowly bubbled in for 20 min. The reddish-brown solution was stirred at 0 °C for 3 h and concentrated in vacuo to give a light-green solid which was washed with cold hexane and filtered giving 22.73 g (0.105 mol, 27%) of 1-oximino-9-chloro-10-methyldecalin, mp 128–132 °C (dec). The filtrate was concentrated in vacuo to give a dark oil which was chromatographed on a 6.5 × 34.5 cm column of silicic acid (Mallinckrodt, Silic Ar, CC-7) slurry packed in 10% chloroform in hexane. Elution in 500-mL fractions gave fraction 1, 1.38 g of unidentified oil, and fractions 2–4, 25.05 g (0.102 mol, 26%) of **5**: NMR ($CDCl_3$) δ 3.30–1.00 (m, 14 H, aliphatic) and 1.11 (s, 3 H, methyl); IR ($CHCl_3$) 6.19, 6.38, and 6.90 μm.

Anal. Calcd for $C_{11}H_{17}N_2O_2Cl$: C. 53.99; H, 7.00; N, 11.45. Found: C, 54.22; H, 7.16; N, 11.11.

1-Nitrimino-9-chloro-10-methyldecalin (5). A solution of 22.73 g (0.105 mol) of 1-oximino-9-chloro-10-methyldecalin in 1.5 L of methylene chloride at 0 °C was stirred while nitrosyl chloride was slowly bubbled in for 30 min. The reddish-brown solution was stirred at 0 °C for 5.5 h, poured into water, washed with water and brine, dried, filtered, and concentrated in vacuo to give a yellow oil which was chromatographed on a 3.5 × 39.5 cm column of silicic acid (Mallinckrodt, Silic AR, CC-7) slurry packed in 10% chloroform in hexane. Elution in 200-mL fractions gave fraction 1, nil, fractions 2–5, 14.49 g (0.059 mol, 56%) of **5**, and fraction 6, 160 mg.

A small sample of **5** was recrystallized from ethanol, yielding white crystals which melted at 61–62 °C.

1-Nitramino-9-chloro-10-methyldecalin (6). Sodium borohydride reduction as above of **5** gave a white solid which was washed with hexane, filtered, and vacuum dried giving a 70% yield of **6** as a white solid: mp 136 °C (dec); NMR ($CDCl_3$) δ 9.10–8.50 (br m, 1 H >NH), 4.76–4.49 (br m, 1 H, $>CH-NHNO_2$), 2.68–0.84 (m, 14 H, aliphatic), and 1.20 (s, 3 H, methyl); IR ($CHCl_3$) 6.24, 6.38, 6.74, and 6.84 μm.

Anal. Calcd for $C_{11}H_{19}N_2O_2Cl$: C, 53.55; H, 7.76; N, 11.35; Cl, 12.97. Found: C, 53.52; H, 7.62; N, 11.30; Cl, 12.99.

1-Chloro-1-(α-nitraminoethyl)cyclohexane (8). Sodium borohydride reduction as above of **7**[1] gave a yellow oil which crystallized from hexane. Recrystallization from hexane afforded a 41% yield of **8** as a white solid: mp 84–85 °C (lit.[1] mp 91–92.5 °C). Both NMR and IR were in agreement with reported spectra.[1]

Registry No.—Acetic acid, 64-19-7; sodium borohydride, 16940-66-2; 2-methyl-2-butene, 513-35-9; nitrosyl chloride, 2696-92-6; 3-chloro-3-methyl-2-butanone oxime, 3238-16-2; 10-methyl-$\Delta^{1,9}$-octalin, 13942-77-6; 1-oximino-9-chloro-10-methyletacalin, 63215-94-1.

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Total Synthesis of (±)-Damsin

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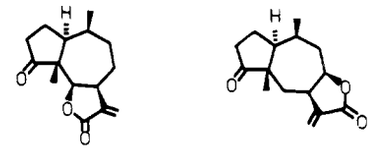
Among the many isolated sesquiterpene lactones[2a] the nonisoprenoid hydroazulenic pseudoguaianolides[2b] represent the largest family. Several synthetic approaches[3–5] to these compounds have appeared, recently culminating in the total syntheses of (±)-damsin[6] (**1**) and (±)-confertin[7] (**2**). In this



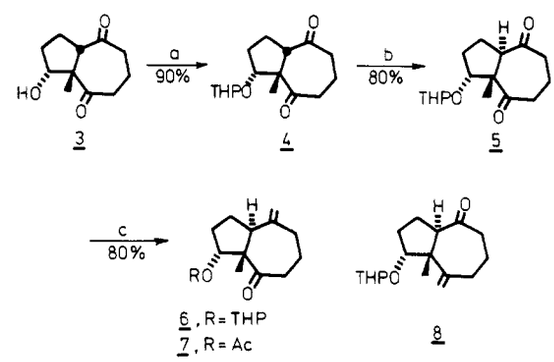
1 **2**

paper we report an independent synthesis of (±)-damsin and describe some transformations of synthon **3** which could be of value for the synthesis of other pseudoguaianolides.

Our synthetic plan centers about the hydroazulenic dione **3**, which we prepared via oxidative cleavage of a tricyclo[5.3.0.$0^{6,10}$]decanetriol.[5,8] This intermediate seems ideally suited for further transformation to pseudoguaianolides. The necessary trans ring fusion of the natural representatives is favored in an equilibrium isomerization process.[9] The two carbonyl functions are expected to be easily differentiated due to a marked difference in steric environment. The hydroxyl group allows for further functionalization of the cyclopentane ring; its α-orientation could, however, disturb the exercise of the stereochemical control by the angular methyl group.[4,10]

The isomerization of compound **4** could easily be achieved in alkaline medium (Scheme I). The equilibrium (85% trans, 15% cis) is largely in favor of the trans ring-fused product, which can be separated from the contaminating dione **4** by crystallization. The presence of a cis-fused γ-butyrolactone in many pseudoguaianolides, e.g., in damsin (**1**), demands alkylation in the 5 position after protection or transformation of the 2-carbonyl function. It has been suggested[4] that the alkylation of similar trans-fused hydroazulenic ketones with methyl bromoacetate proceeds poorly, unless one or more additional trigonal centers are present in the enolate, thereby lowering the steric congestion of the seven-membered ring. These considerations coupled with the anticipated formation of a β-methyl group on catalytic hydrogenation of an *exo*-methylene function led us to synthesize ketone **6**. Under the

Scheme I[a]



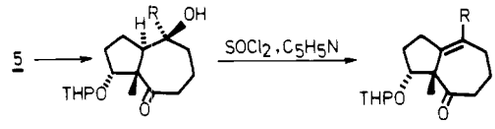
3 **4** **5**

6, R = THP
7, R = Ac

8

[a] a, DHP, *p*-TsOH; b, NaOH, MeOH; c, $(C_6H_5)_3P{=}CH_2$, THF.

given reaction conditions (Scheme I) the olefin **6** was obtained from diketone **5** in high yield and as the sole product. When Me_2SO was used as solvent, attack at the more hindered 6-ketone function, leading to product **8**, also occurred.[11] In



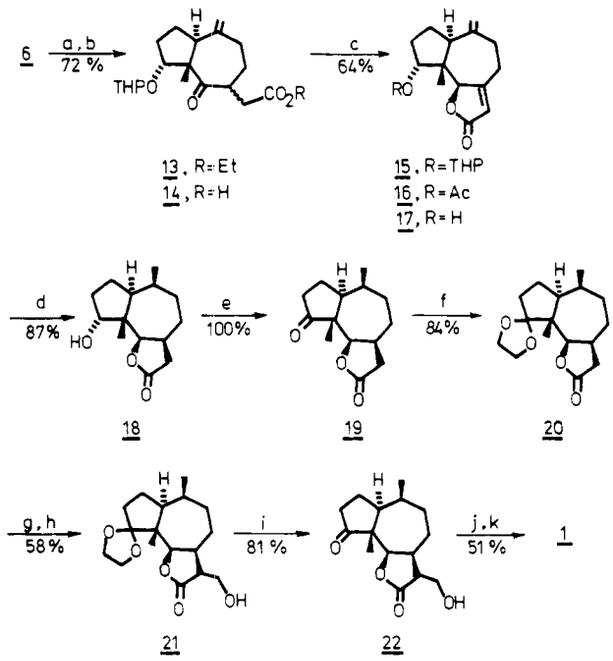
9, R = Me
10, R = H

11, R = Me
12, R = H

preliminary experiments a regioselective methyllithium reaction on **5**, followed by dehydration, was attempted. The reaction with methyllithium, although mostly regioselective, gave a low yield of the tertiary alcohol **9**; it is interesting to note that subsequent dehydration with thionyl chloride–pyridine gave nearly exclusively the tetrasubstituted olefin **11**, indicating a quasi-trans-diaxial relationship between the ring fusion hydrogen and the hydroxyl group.[12] A similar result was obtained when the alcohol **10**, from the reduction of **5** with lithium tri-*tert*-butyloxyaluminum hydride, was treated with thionyl chloride–pyridine.

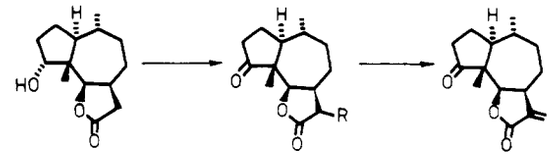
The further conversion of ketone **6** to damsin (**1**) was performed in a straightforward way (Scheme II). Following the concept of Marshall[4,7] we decided to introduce the thermodynamically less favored orientation of the ester side chain through catalytic hydrogenation of the butenolide **15**. This product was obtained in a three-step sequence, involving alkylation of unsaturated ketone **6** with ethyl bromoacetate, saponification of the resulting epimeric mixture **13** to the keto acids **14**, and finally, treatment with acetic anhydride–sodium acetate.[13] Analysis of the ^1H NMR spectra of the corresponding alcohol **17** and its acetate **16** clearly shows butenolide **15** being stereohomogeneous (except for the chirality present in the protective ether group); the stereochemistry shown at C-6 could not be established at this point. In order to minimize

Scheme II[a]



[a] a, LDA, $BrCH_2CO_2Et$, HMPA; b, KOH, MeOH; c, Ac_2O, NaOAc; d, H_2, Pt/C(10%), EtOH; e, H_2CrO_4, acetone; f, $(CH_2OH)_2$, *p*-TsOH; g, NaH, HCO_2Et; h, $NaBH_4$, MeOH; i, 3 M HCl, MeOH; j, *p*-TsCl, C_5H_5N; k, C_5H_5N.

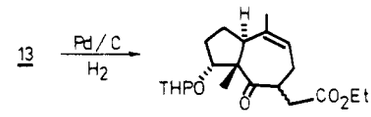
the steric influence of the 8α ether group it was decided to perform the catalytic hydrogenation at this stage and not earlier; indeed, the anticipated faster reduction of the enone system would provide us with a trans-fused hydroazulene possessing an almost inaccessible β face. The catalytic hydrogenation on 5% platinum on carbon gave as sole reduction products the alcohol **18** and the isomeric product at C-2 **18a** (85:15, respectively), with concomitant cleavage of the protective ether group.[14] Isomer **18a** was not separated at this



18a **19a**, R = H; **22a**, R = CH_2OH **1a**

stage, but was taken through the remaining reaction sequence. Jones oxidation led to the cyclopentanones **19** and **19a**. The former lactone has already been synthesized and transformed into (±)-damsin[6] (**1**). Our present synthesis was completed using the same six-step reaction sequence, yielding (±)-damsin (**1**) and its C-2 epimer[15] (**1a**); both compounds were easily separated on silica gel. The spectral properties and TLC behavior of the synthetic material were identical with naturally occurring damsin[16] (**1**).

We are currently investigating the further potentiality of products **6**, **11**, and **12** for the synthesis of other pseudoguaianolides. In this context we also want to report the accidental formation of the trisubstituted olefin **23** in high yield



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during an attempted catalytic hydrogenation of ester **13** using 5% palladium on carbon; this ester looks promising for the functionalization of the 4 position, which is often encountered in pseudoguaianolides.

Experimental Section[17]

***c*-7-Methyl-*t*-8-(2′-tetrahydropyranyloxy)-*r*-1*H*-bicyclo-[5.3.0]decane-2,6-dione (4).** A solution of 4.50 g (23 mmol) of hydroazulenol **3**, 9.5 mL (104 mmol) of dihydropyran, and 15 mg of *p*-toluenesulfonic acid in 100 mL of methylene chloride was stirred at room temperature for 15 min. The reaction solution was quenched with solid potassium carbonate, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using 10% ethyl acetate–benzene, yielding 5.78 g (90%) of the dione **4** as a light yellow oil: R_f (2) 0.51; IR (film) 1700, 1220, 1210, 1130, 1030, 990 cm^{-1}; NMR δ_{Me_4Si} 4.20–4.05 (m, C-8 methine), 2.90–2.20 (m, C-1, C-3, and C-5 H), 1.35 and 1.33 (s, C-7 CH_3); MS *m/e* 196 (40), 179 (10), 152 (6), 151 (5), 85 (100). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.69; H, 8.71.

***t*-7-Methyl-*c*-8-(2′-tetrahydropyranyloxy)-*r*-1*H*-bicyclo-[5.3.0]decane-2,6-dione (5).** A solution of 5.78 g (20.6 mmol) of cis-ring-fused diketone **4** in 100 mL of dry methanol containing 15 mg of powdered sodium hydroxide was stirred at room temperature for 70 h. After evaporation of the solvent, workup yielded 5.70 g of a semisolid product (85% **5**; 15% **4**). White crystalline diketone **5** (yield 80%; conversion 100%) was obtained by recrystallization from isooctane: R_f (2) 0.51; IR (KBr) 1700, 1130, 1030, 1025, 990 cm^{-1}; NMR δ_{Me_4Si} 4.30–4.10 (m, C-8 methine), ~3.9 (m, C-1 methine), 0.93 and 0.87 (s, C-7 CH_3); MS *m/e* 280 (M^+, 2), 262 (1), 196 (100), 179 (92), 161 (65), 152 (61), 85 (100), 67 (96), 41 (100). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.72; H, 8.72.

***t*-7-Methyl-2-methylene-*c*-8-(2′-tetrahydropyranyloxy)-*r*-1*H*-bicyclo[5.3.0]decan-6-one (6).** To a suspension of methylene triphenylphosphorane (from 8.93 g, 25 mmol of methyltriphenylphosphonium bromide and 12.5 mL of 2.0 M butyllithium–hexane solution) in 30 mL of tetrahydrofuran was added a solution of 1.44

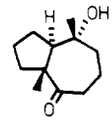
g (5.13 mmol) of dione **5** in 5 mL of tetrahydrofuran at room temperature. After 15 min the reaction mixture was poured into a saturated ammonium chloride solution. Workup and purification by column chromatography on silica gel using 6% ethyl acetate–benzene yielded 1.13 g (80%) of a colorless oil: R_f (2) 0.66; IR (film) 3100, 1700, 1650, 1125, 1115, 1060, 1020, 985 cm^{-1}; NMR δ_{Me_4Si} 5.03 and 4.86 (s, *exo*-CH_2 vinyl H's), 4.27 and 4.13 (m, C-8 methine), 2.6–2.3 (m, C-5 CH_2), 3.3 (t, J = 8.4 Hz, C-1 methine), 0.93 and 0.87 (s, C-7 CH_3); MS *m/e* 194 (30), 85 (100). Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.51; H, 9.43.

The ^1H NMR spectrum of the reaction mixture from the same reaction using dimethyl sulfoxide as solvent showed the presence of the isomeric ketone **8**: NMR δ_{Me_4Si} 4.83 (s, *exo*-CH_2 vinyl H's) and 1.23 (s, C-7 CH_3).

The stereohomogeneous acetate **7** was isolated accidentally upon treatment of **6** with acetic anhydride and a trace of perchloric acid (70%) in carbon tetrachloride: R_f (1) 0.43; IR (KBr) 1750, 1700, 1240 cm^{-1}; NMR δ_{Me_4Si} 5.20 (m, C-8 methine), 5.10 and 4.92 (s, *exo*-CH_2 vinyl H's), 3.36 (t, J = 9.0 Hz, C-1 methine), 2.0 (s, $OCOCH_3$), 1.00 (s, C-7 CH_3); MS *m/e* 236 (M^+, 2), 194 (36), 176 (70), 161 (22), 150 (29), 137 (57), 43 (100).

c-2,t-7-Dimethyl-t-2-hydroxy-c-8-(2′-tetrahydropyranyloxy)-r-1H-bicyclo[5.3.0]decan-6-one (9). To a solution of 2.10 g (7.5 mmol) of diketone **5** in 6 mL of tetrahydrofuran was added 3.5 mL of a 2.12 M methyllithium–ether solution at room temperature. Stirring was continued for 2 h, the reaction mixture poured on ice, and the product isolated with ether. Purification by column chromatography on silica gel with 20% ethyl acetate–benzene yielded 0.356 g (83% conversion) of starting material and 0.694 g (38%) of alcohol **9** as a colorless oil: R_f (1) 0.30; IR (film) 3500, 1695, 1125, 1025, 990 cm^{-1}; NMR δ_{Me_4Si} 1.33 (s, C-2 CH_3) and 1.17, 1.14 (s, C-7 CH_3); MS *m/e* 296 (M^+, 0.4), 212 (20), 195 (20), 168 (98), 85 (100).

2,t-7-Dimethyl-r-8-(2′-tetrahydropyranyloxy)bicyclo[5.3.0]-dec-1,2-en-6-one (11). A solution of 0.225 g (0.76 mmol) of alcohol **9** and 0.25 g (0.154 mL) of thionyl chloride in 2 mL of pyridine was stirred at room temperature for 12 h. The reaction mixture was poured into ice water and isolated with pentane, yielding 0.168 g (79%) of tetrasubstituted olefin **11** as a pale yellow oil: R_f (1) 0.56; IR (film)



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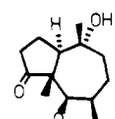

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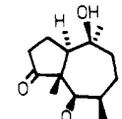

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1700, 1125, 1110, 1020, 980 cm^{-1}; NMR δ_{Me_4Si} 1.80 (s, C-2 CH_3) and 1.19, 1.15 (s, C-7 CH_3); MS *m/e* 278 (M^+, 1), 194 (28), 85 (100). Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.54; H, 9.45.

t-2-Hydroxy-t-7-methyl-c-8-(2′-tetrahydropyranyloxy)-r-1H-bicyclo[5.3.0]decan-6-one (10). To a suspension of 29 mg (7.6 mmol) of lithium aluminum hydride in tetrahydrofuran was added 0.28 mL of *tert*-butyl alcohol at 0 °C. Stirring was continued for 30 min and a solution of 105 mg (0.38 mmol) of the diketone **5** in tetrahydrofuran was added dropwise over 2 min at 0 °C. After 30 min the reaction mixture was poured into a saturated ammonium chloride solution and the product isolated with ether, yielding 100 mg (93%) of a colorless oil: R_f (1) 0.26; IR (film) 3500, 1700, 1030, 990 cm^{-1}; NMR δ_{Me_4Si} 1.22 and 1.18 (s, C-7 CH_3); MS *m/e* 198 (18), 154 (52), 85 (100). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.08; H, 9.22. Found: C, 68.26; H, 9.25.

t-7-Methyl-r-8-(2′-tetrahydropyranyloxy)bicyclo[5.3.0]-dec-1,2-en-6-one (12). The above mentioned procedure with thionyl chloride–pyridine on 100 mg (0.35 mmol) of the alcohol **10** yielded crude trisubstituted olefin **12** as a pale yellow oil: R_f (1) 0.54; IR (film) 1705, 1125, 1110, 1030, 1020, 980 cm^{-1}; NMR δ_{Me_4Si} 5.7 (m, vinyl H), 1.20 (s, C-7 CH_3); MS *m/e* 264 (M^+, 1), 246 (2), 216 (2), 85 (100).

Ethyl [2-Methylene-6-oxo-t-7-methyl-c-8-(2′-tetrahydropyranyloxy)-r-1H-bicyclo[5.3.0]dec-5-yl]acetate (13). The procedure described by Marshall[4] was slightly modified. To a solution of 0.924 mL (6.6 mmol) of *N,N*-diisopropylamine in 10 mL of tetrahydrofuran was added at −78 °C 3.3 mL (6.6 mmol) of 2.0 M *n*-butyllithium–hexane solution dropwise over 2.0 min. The temperature was raised to 0 °C over 30 min. A solution of 0.911 g (3.3 mmol) of ketone **6** in 2 mL of tetrahydrofuran was added at −78 °C and stirring was continued for 3 h at room temperature. Finally, a solution of 0.8 mL (7.2 mmol) of ethyl bromoacetate and 1.26 mL (7.2 mmol) of hexamethylphosphoric triamide in 4 mL of tetrahydrofuran was added (−78 °C). Stirring was continued for 30 min and the reaction mixture poured into a saturated ammonium chloride solution. Workup and purification by column chromatography on silica gel using 25% ethyl acetate–isooctane yielded 0.964 g (80%) of **13** (light yellow oil): R_f (2) 0.67; IR (film) 3100, 1740, 1700, 1640, 1195, 1170, 1125, 1110, 1075, 1030, 1020, 985, 830 cm^{-1}; δ_{Me_4Si} 5.13 and 4.96 (s, *exo*-CH_2 vinyl H's), 4.16 (q, J = 7.3 Hz, $COOCH_2CH_3$), 1.26 (t, J = 7.3 Hz, $COOCH_2CH_3$), 0.92 and 0.88 (s, C-7 CH_3); MS *m/e* 280 (10), 251 (10), 217 (18), 213 (40), 185 (55), 85 (100).

[2-Methylene-t-7-methyl-c-8-(2′-tetrahydropyranyloxy)-6-oxo-r-1H-bicyclo[5.3.0]dec-5-yl]acetic Acid (14). A solution of 0.70 g (1.92 mmol) of ester **13** and 0.40 g (7.1 mmol) of potassium hydroxide in 10 mL of dry methanol was heated at reflux for 2 h. The solution was cooled and concentrated in vacuo. Water was added to the residue and the solution was acidified to pH 4 with 1.2 M hydrochloric acid. Workup yielded 0.61 g (90%) of **14** as semisolid oil: R_f (2) 0.55; R_f (1) 0.39; IR (melt) 3200–2500 (br), 1750–1700, 1650 cm^{-1}; NMR δ_{Me_4Si} 5.03 and 4.86 (s, *exo*-CH_2 vinyl H's), 2.55 (m, CH_2COOH), 0.9 (s, C-7 CH_3), 9.5 (COOH); MS (*m/e* 250 (40), 217 (20), 195 (8), 177 (10), 85 (100). Anal. Calcd for $C_{19}H_{28}O_5$: C, 67.83; H, 8.39. Found: C, 67.89; H, 8.41.

[2-Methylene-t-6-hydroxy-t-7-methyl-c-8-(2′-tetrahydropyranyloxy)-r-1H-bicyclo[5.3.0]dec-5-ylidene]acetic Acid γ-Lactone (15). A mixture of 0.60 g (1.78 mmol) of acid **14** and 2.16 g (26.3 mmol) of sodium acetate in 18 mL of acetic anhydride was heated at reflux for 1 h. The mixture was cooled to 0 °C and 20 mL of methanol was added. The solution was stirred for 2 h at 0 °C and then poured into water and the product extracted with ether. The product was freed from acetic acid by azeotropic distillation in vacuo with toluene. Purification by column chromatography on silica gel using 30% ethyl acetate–isooctane yielded 0.36 g (64%) of butenolide **15** as a white crystalline product: R_f (2) 0.54; IR (KBr) 3100, 1770, 1640 cm^{-1}; δ_{Me_4Si} 5.86 (m, vinyl H), 5.63 and 5.43 (s, C-6 methine), 5.03 and 4.90 (s, *exo*-CH_2 vinyl H's), 0.46 and 0.43 (s, C-7, CH_3), MS *m/e* 318 (M^+, 0.8), 234 (30), 217 (44), 216 (50), 85 (100).

Prolonged reaction times and careless (temperature!) workup lowered the yield and led in preliminary experiments to considerable amounts of the corresponding acetate **16** (mp 125–126 °C): IR (KBr) 3100, 1760, 1740, 1650, 1640, 1250 cm^{-1}; NMR δ_{Me_4Si} 5.88 (q, J = 1.8 Hz, vinyl H), 5.40 (s, C-6 methine), 5.08 and 4.93 (s, *exo*-CH_2 vinyl H's), 5.02 (m, C-8 methine), 2.10 (s, $OCOCH_3$), 0.50 (s, C-7 CH_3); MS *m/e* 276 (M^+, 2), 234 (20), 216 (70), 43 (100).

The corresponding hydroxy derivative **17** showed δ_{Me_4Si} 5.85 (q, J = 1.8 Hz, vinyl H), 5.43 (s, C-6 methine), 5.03 and 4.90 (s, *exo*-CH_2 vinyl H's), 4.16 (m, C-8 methine) and 0.41 (s, C-7 CH_3).

(t-2,t-7-Dimethyl-t-6,c-8-dihydroxy-r-1H-bicyclo[5.3.0]-dec-5-yl)acetic Acid γ-Lactone (18). A suspension of 0.36 g (1.13 mmol) of butenolide **15** and 120 mg of 5% platinum on carbon in 6 mL of absolute ethanol was hydrogenated at room temperature under a pressure of 4 bar. After 70 h the reaction mixture was filtered and concentrated in vacuo, yielding 0.233 g (87%) of lactone (**18** and **18a**) as a white crystalline solid: R_f (2) 0.39; IR (KBr) 3500, 1780, 1180, 1040, 1010, 990 cm^{-1}; NMR δ_{Me_4Si} 4.96 (d, J = 9.3 Hz, C-6 methine), 3.86 (m, C-8 methine), 1.05 (d, j, 7.2 Hz, C-2 CH_3), 0.93 (s, C-7 CH_3); MS *m/e* 238 (M^+, 4), 236 (2), 220 (52), 205 (83), 179 (60), 41 (100). The contaminating isomer **18a** showed δ_{Me_4Si} 3.96 (m, C-8 methine) and 0.85 (s, C-7 CH_3).

(t-2,t-7-Dimethyl-8-oxo-t-6-hydroxy-r-1H-bicyclo[5.3.0]-dec-5-yl)acetic Acid γ-Lactone (19). To a solution of 0.233 g (0.96 mmol) of alcohol **18** in 10 mL of acetone was added at −15 °C Jones reagent till the red color persisted. The mixture was quenched with isopropyl alcohol, solid sodium hydrogen carbonate added, and the mixture filtered and concentrated in vacuo. Usual workup yielded 0.230 g of ketone (100%) as a colorless oil which solidified on standing. Recrystallization from diisopropyl ether gave analytically pure material (mp 133–134 °C): R_f (2) 0.29; IR (melt) 1750, 1765 cm^{-1}; δ_{Me_4Si} 4.6 (d, J = 7.2 Hz, C-6 methine), 1.16 (s, C-7 CH_3), 1.10 (d, J = 7.2 Hz, C-2 CH_3); MS *m/e* 236 (M^+, 3), 220 (100), 97 (41). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.32; H, 8.61. The isomeric ketone **19a** showed: R_f (2) 0.33; δ_{Me_4Si} 4.6 (d, 6.0 Hz, C-6 methine), 1.13 (s, C-7 CH_3), and 0.96 (d, 5.7 Hz, C-2 CH_3).

Ethylene Ketal of (t-2,t-7-Dimethyl-t-6-hydroxy-8-oxo-r-1H-bicyclo[5.3.0]dec-5-yl)acetic Acid γ-Lactone (20). A solution of 0.150 g (0.63 mmol) of ketone **19**, 1 mg of *p*-toluenesulfonic acid, and 0.5 mL of ethylene glycol in 10 mL of benzene was heated at reflux for 6 h using a Dean–Stark water separator. The solution was cooled, solid potassium carbonate was added, and the mixture was filtered and concentrated in vacuo. Purification by column chromatography on silica gel using 45% ethyl acetate–isooctane yielded 0.15 g (84%) of lactone **20** (and its C-2 epimer) as a white crystalline solid: R_f (2)

0.50; mp 92–98 °C (from isooctane); IR (KBr) 1770 cm^{-1}; NMR δ_{Me_4Si} 4.96 (d, J = 6.0 Hz, C-6 methine), ~4.0 (m, ketal), 1.12 (s, C-7 CH_3), 1.03 (d, J = 7.2 Hz, C-2 CH_3); MS m/e 280 (M^+), 265, 235, 219, 100, 99, 86. The contaminating C-2 α-CH_3 isomer showed δ_{Me_4Si} 4.96 (d, J = 8.4 Hz), 1.07 (s, C-7 CH_3) and 0.9 (d, J = 5.4 Hz, C-2 CH_3).

Ethylene Ketal of (*t*-2,7-Dimethyl-*t*-6-hydroxy-8-oxo-*r*-1*H*-bicyclo[5.3.0]dec-5-yl)β-hydroxypropionic Acid γ-Lactone (21). The procedure of Minato and Horibe[18] was employed. To a suspension of 76 mg of 55% sodium hydride suspension in 4 mL of ether was added at 0 °C a solution of 0.323 g (1.15 mmol) of lactone **20** and 0.17 mL (2 mmol) of ethyl formate in 4 mL of ether dropwise over 2 min. The suspension was stirred for 1 h at 0 °C and for an additional 7 h at room temperature. The reaction mixture was poured into a saturated ammonium chloride solution and extracted with ether. Workup yielded 0.342 g (97%) of crude product; no purification of this product was attempted.

To a solution of 50 mg (1.31 mmol) of sodium borohydride in 3 mL of absolute methanol was added at −18 °C a solution of 0.342 g (1.11 mmol) of the above α-formyl-γ-butyrolactone in 2 mL of absolute methanol. The solution was stirred at −18 °C for 1 h, slowly brought to room temperature, and poured into a saturated ammonium chloride solution. The product was isolated with ether and purified by column chromatography on silica gel using 50% ethyl acetate–isooctane, yielding 0.206 g (60%) of a white crystalline solid: R_f (2) 0.34; NMR δ_{Me_4Si} 4.93 (d, J = 9.3 Hz, C-6 methine), ~3.9 (m, ethylene ketal), ~3.8 (m, CH_2OH), 1.10 (s, C-7 CH_3), 1.06 (d, J > 6.6 Hz, C-2 CH_3). The contaminating C-2 α-CH_3 isomer showed δ_{Me_4Si} 1.06 (s, C-7 CH_3) and 0.90 (d, J = 5.4 Hz, C-2 CH_3).

(*t*-2,7-Dimethyl-8-oxo-*t*-6-hydroxy-*r*-1*H*-bicyclo[5.3.0]-dec-5-yl)-β-hydroxypropionic Acid γ-Lactone (22). A solution of 0.206 g (0.66 mmol) of ethylene ketal **21** in 5 mL of 40% 3 M hydrochloric acid–methanol was stirred at 0 °C for 15 min. Methanol was evaporated in vacuo, water was added, and the product extracted with ether. Isolation and purification by column chromatography on solica gel using 25% isooctane–ethyl acetate yielded 0.144 g (81%) of **22** as a colorless oil: R_f (2) 0.13; NMR δ_{Me_4Si} 4.56 (d, J = 8.7 Hz, C-6 methine), 4.1 (m, $CHCH_2OH$), 3.9 (m, CH_2OH), 2.9 (m, C-5 methine), 1.13 (s, C-7 CH_3), 1.07 (d, C-2 CH_3); MS m/e 266 (M^+, 2), 251 (100), 233 (25), 97 (50). The isomeric ketone **22a** showed: R_f (2) 0.17; δ_{Me_4Si} 4.66 (d, J > 7.2 Hz, C-6 methine), 1.09 (s, C-7 CH_3), 1.00 (d, J = 5.4 Hz, C-2 CH_3).

(±)-Damsin (1). A solution of 0.144 g (0.54 mmol) of the above β′-hydroxy-γ-butyrolactone **22** and 126 mg of *p*-toluenesulfonyl chloride in 1.6 mL of freshly distilled pyridine was stirred for 24 h at 0 °C. The solution was poured into water and the product isolated with chloroform, yielding 0.227 g (100%) of a yellow oil. A solution of the above crude tosylate in 2 mL of pyridine was heated at reflux for 4 h. The solution was cooled and poured into water; extraction with ether and evaporation of the solvent gave 0.134 g (100%) of yellow oil. Purification by column chromatography on silica gel using 50% ethyl acetate–isooctane yielded 73 mg (51%) of white crystalline product, whose spectra and TLC behavior were identical with those of naturally occurring damsin (1): R_f (2) 0.35; mp 122–124 °C; IR (KBr) 2950, 2875, 1760, 1735, 1655, 1280, 1165, 1155, 1130, 1060, 1000, 985, 970, 955, 820 cm^{-1}; NMR δ_{Me_4Si} 6.27 and 5.53 (d, J = 3.1 and 2.75 Hz, respectively, vinyl H's), 4.53 (d, J = 8.5 Hz, C-6 methine), 3.30 (m, C-7 methine), 1.08 (d, J = 7.5 Hz, C-2 CH_3), 1.08 (s, C-7 CH_3); MS m/e 248 (M^+, 5), 2.33 (100), 123 (36), 97 (42), 95 (30), 55 (50). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.61; H, 8.14.

(±)-2-*epi*-Damsin (**1a**), contaminated with (±)-damsin (a fraction of the above mentioned column chromatography), was purified by preparative TLC using 50% ethyl acetate–isooctane, affording 2 mg of white crystalline compound: R_f (2) 0.41; NMR δ_{Me_4Si} 6.26 and 5.57 (d, J = 2.5 and 2.0 Hz, respectively, vinyl H's), 4.53 (d, J = 7.75 Hz, C-6 methine), 3.11 (m, C-7 methine), 1.00 (d, J = 6.5 Hz, C-2 CH_3), 1.11 (s, C-7 CH_3).

Ethyl [2,*t*-7-Dimethyl-*c*-8-(2′-tetrahydropyranyloxy)-6-oxo-*r*-1*H*-bicyclo[5.3.0]dec-2-en-5-yl]acetate (23). A suspension of 0.364 g (1.0 mmol) of olefin **13** and 10 mg of 5% palladium on carbon in 1 mL of absolute ethanol was hydrogenated at room temperature and atmospheric pressure. After 6 h the suspension was filtered and concentrated in vacuo, yielding 0.362 g (100%) of trisubstituted olefin **23**: R_f (1) 0.49; IR (film) 1740, 1700, 1195, 1175, 1160, 1130, 1115, 1025, 985 cm^{-1}; NMR δ_{Me_4Si} 5.83 (m, vinyl H), 4.20 (q, J = 7.2 Hz, $COOCH_2CH_3$), 1.26 (t, J = 7.2 Hz, $COOCH_2CH_3$), 0.95 (s, C-7 CH_3).

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Thermal Decomposition of Phenylmethyldiazirine. Effect of Solvent on Product Distribution

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The thermal decomposition of phenyl-*n*-butyldiazirine[1] in Me_2SO at 100 °C resulted in a quantitative evolution of nitrogen and the formation of *cis*- and *trans*-1-phenyl-1-pentenes plus less than 5% of valerophenone. In addition, 1-phenyldiazopentane has been isolated as an intermediate