Total Synthesis of (±)-Sarracenin

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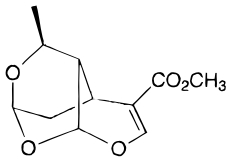
A total synthesis of (±)-sarracenin (**1**) is described. The key steps include (1) regioselective ring expansion of **7** to bicyclo[3.2.1]ketone **6** and (2) ring opening of tricyclic ketone **5** to ester **4**.

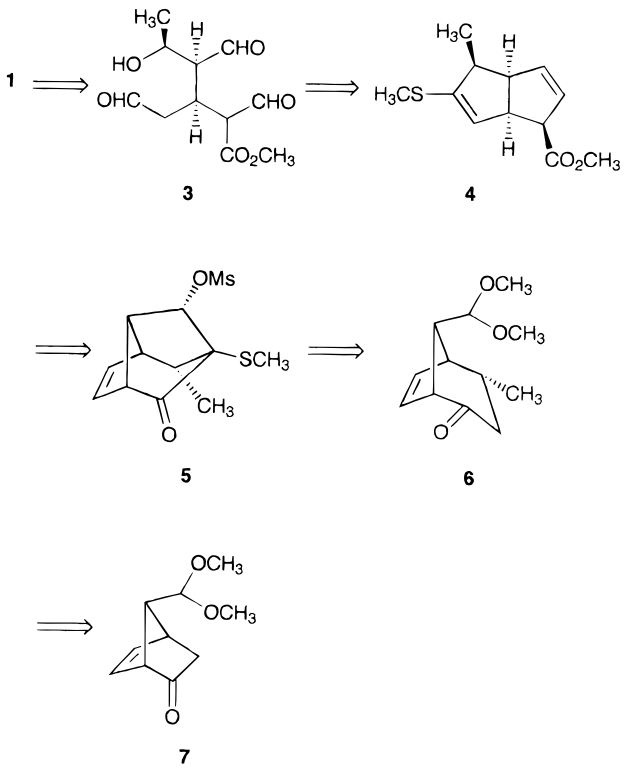
Sarracenin (**1**) is a highly oxygenated and densely functionalized tricyclic monoterpene, which has been isolated from *Sarracenia flava*.[1] It was proposed that sarracenin is a likely component in the synthesis of biosynthetically related compounds, such as secologanin and ajmalicine.[1] These characteristics make sarracenin an attractive target for synthesis.[2] In this report, we describe a new total synthesis of recemic sarracenin.



Sarracenin (**1**)

Our approach was based on the transformation of a readily available bicyclo[2.2.1]heptanone **7**[3] into trialdehyde **3**, which was reported to form sarracenin on treatment with acid.[4] As shown in Scheme 1, the key steps of the present synthesis include (1) regioselective ring expansion of **7** to bicyclo[3.2.1]ketone **6** and (2) ring opening of tricyclic ketone **5** to ester **4**.

Scheme 1



Results and Disscussion

The synthesis began (see Scheme 2) with methylation of ketone **7**, which was effected by deprotonation with lithium diisopropylamide and treatment with methyl iodide. Workup gave rise to a 20:1 mixture, the major constituent of which was formulated as **8** based on the expectation that steric shielding by C-7 substituent would favor the approach of the alkylating agent from the endo face of the molecule. Regioselective ring expansion of **8** was accomplished as follows. Treatment of **8** with dimethylsulfoxonium methylide, followed by ammonolysis of the resulting epoxide, gave a β-amino alcohol. Without purification, reaction of the β-amino alcohol with nitrous acid furnished the ring-expanded ketone **6**.[5] With ketone **6** in hand, the synthesis of the key intermediate tricyclic ketone **5** was next examined. Ketone **6** was first transformed to thioether **9**.[6] On treatment with aqueous acid, **9** was converted to β-hydroxy ketone **10**, which then reacted with methanesulfonyl chloride in pyridine to give the corresponding mesylate **5**.[7] The relative and absolute stereochemistries of this product were confirmed by single-crystal X-ray analysis.[11]

With a viable approach to tricyclic ketone **5** assured, we turned our attention to the formation of **14**, a reasonable precursor of trialdehyde **3**. Reaction of **5** with potassium hydroxide followed by acid workup produced diene acids. Without purification, these acids were treated with diazomethane to yield ester **13** as the major product accompanied with a trace amount of isomer **4** as judged by its ^{1}H NMR spectrum. This result was unexpected. Apparently, once the acid **11** was formed, a double bond isomerization proceeded under the acid medium. Hydrolysis of the vinyl sulfide functionality in the mixture of **4** and **13** with mercury(II) chloride[8] provided a ca. 1.3:1 ratio of C-8 epimers, with desired **14** predominating. Epimerization of **15** to **14** was achieved

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(7) Chang, C. P.; Hsu, L. F.; Chang, N. C. *J. Org. Chem.* **1994**, *59*, 1898.

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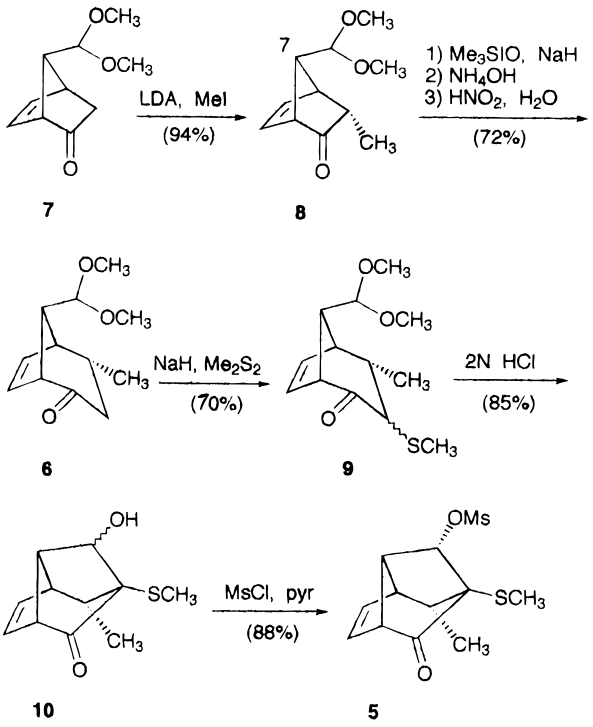
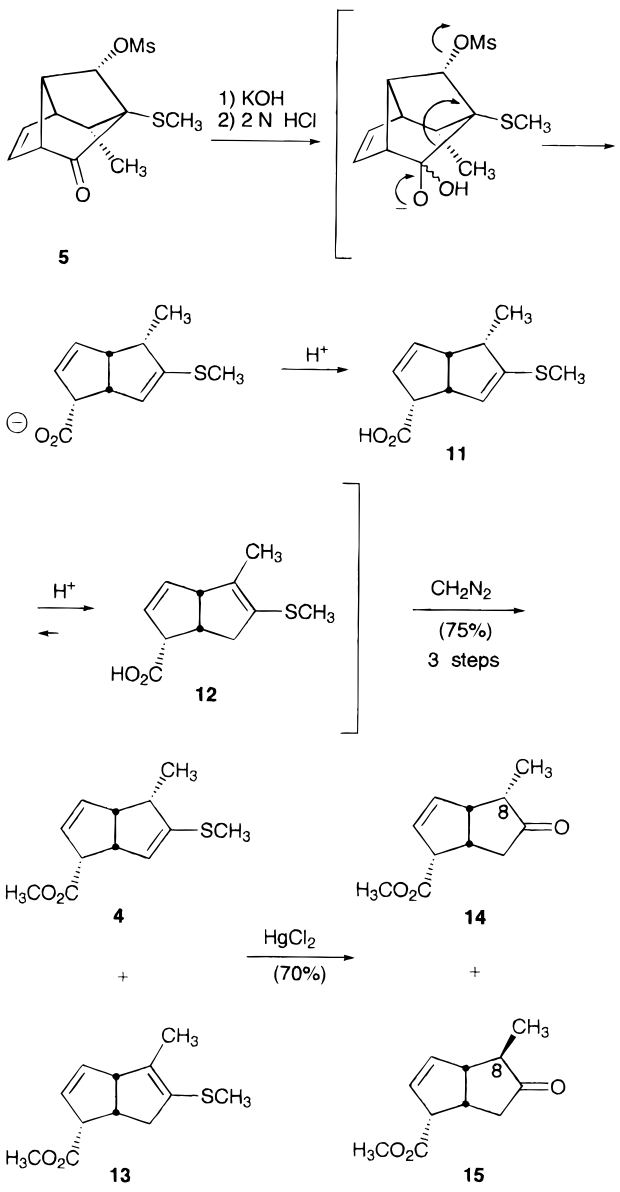
Scheme 2



Scheme 3



simply by quenching the dienolate, resulting from reaction of **15** with lithium diisopropylamide, with aqueous acetic acid solution at 25 °C.[9]

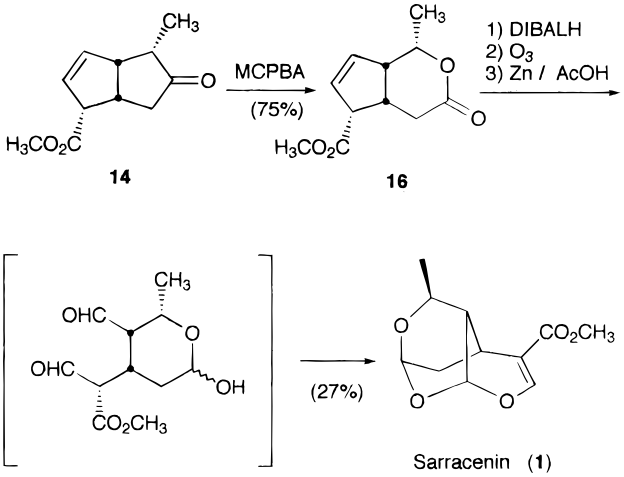
Final conversion of enone **14** to sarracenin was then accomplished *via* the protocol employed by Whitesell in their successful synthesis.[2f] Baeyer−Villiger oxidation of **14** furnished lactone **16**. The structure of **16** was confirmed by X-ray analysis.[11] Reaction of **16** with diisobutylaluminum hydride afforded the corresponding lactol. Treatment of the crude lactol with ozone, reduction of the ozonide with zinc in acetic acid, and dehydrative cyclization in the same acid medium produced (±)-sarracenin (**1**) (mp = 107−108 °C) in 27% overall yield from **16**. The ^{1}H and ^{13}C NMR spectra of **1** are identical to those reported by Professor Whitesell.[10] The above procedure constitutes a new approach to the synthesis of sarracenin (**1**).

Experimental Section

General Methods. Diethyl ether and tetrahydrofuran (THF) were distilled prior to use from a deep-blue solution of sodium benzophenone ketyl. All other reagents and solvents were obtained from commerical sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Solutions of products in organic solvents were dried with anhydrous $MgSO_4$ before concentration *in vacuo*. Crude products were purified by preparative TLC or column chromatography on silica gel. All reported temperatures are uncorrected. The purity of all titled compounds was established to be >90% by inspection of ^{1}H and ^{13}C NMR spectra unless otherwise stated.

***endo*-3-Methyl-*syn*-7-(dimethoxymethyl)bicyclo[2.2.1]-hept-5-en-2-one (8).** To a solution of lithium diisopropylamide, prepared from 8.1 mL (57.7 mmol) of diisopropylamine in 150 mL of freshly distilled tetrahydrofuran and 34.4 mL (54.9 mmol) of *n*-butyllithium (1.6 M in hexane) at −78 °C, was added a solution of 5.0 g (27.5 mmol) of keto ketal **7** in 15 mL of tetrahydrofuran. After this mixture was stirred for an additional 30 min at −78 °C, 4.3 mL (68.7 mmol) of methyl

Scheme 4



(9) Trost, B. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1985**, *107*, 1293.

(10) We thank Professor J. K. Whitesell, University of Texas at Austin, for providing us the NMR spectra for comparsion.

(11) The author has deposited atomic coordinates for **5** and **16** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CH2 1EZ, UK.

iodide was added. The reaction mixture was stirred at −78 °C for 1 h, warmed to 25 °C over 1 h, and stirred at 67 °C for an additional 12 h. The reaction was quenched with water, and the solvent was removed under reduced pressure. The residue was taken up with 10 mL of water and was extracted with ethyl acetate (50 × 3 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated to afford crude **8**. Purification on silica gel (elution with 5:1 *n*-hexane/ethyl acetate) afforded 5.05 g (94%) of **8** as a yellowish oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (dd, J = 5.7, 3.0 Hz, 1H), 6.11 (dd, J = 5.7, 4.2 Hz, 1H), 4.32 (d, J = 8.4 Hz, 1H), 3.35 (s, 3H), 3.34 (s, 3H), 3.04−3.03 (m, 1H), 3.00−2.95 (m, 1H), 2.71 (dd, J = 8.1, 1.2 Hz, 1H), 2.25−2.22 (m, 1H), 1.06 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.9, 142.2, 130.5, 102.0, 63.0, 57.5, 54.4, 52.3, 45.9, 38.7, 16.5; IR ($CHCl_3$, cm^{-1}) 3015, 1707; HRMS calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1098.

***endo*-4-Methyl-*syn*-8-(dimethoxymethyl)bicyclo[3.2.1]-oct-6-en-2-one (6).** A suspension of 0.73 g (30.6 mmol) of dry-nitrogen-blanketed sodium hydride in 150 mL of dry tetrahydrofuran and 8.4 g (38.3 mmol) of trimethylsulfoxonium iodide was heated at 67 °C for 4 h. The solution was cooled to 0 °C, and the reaction mixture was stirred for 10 min before 5.0 g (25.5 mmol) of ketone **8** in 5 mL of tetrahydrofuran was added. Stirring was continued at 25 °C for 48 h. The reaction mixture was then diluted with 50 mL of water, and the product was extracted with ethyl acetate (50 × 4 mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$), filtered, and evaporated *in vacuo* to afford a crude product that was purified by flash column chromatography on silica gel (elution with 4:1 *n*-hexane/ethyl acetate) to afford 5.1 g (95%) of epoxy acetal as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (dd, J = 6.0, 3.0 Hz, 1H), 6.20 (dd, J = 6.0, 3.3 Hz, 1H), 4.74 (d, J = 9.3 Hz, 1H), 3.42 (s, 3H), 3.38 (s, 3H), 2.75 (d, J = 4.2 Hz, 2H), 2.63 (d, J = 4.2 Hz, 1H), 2.33−2.29 (m, 2H), 2.23−2.19 (m, 1H), 0.88 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 134.3, 102.4, 69.3, 62.7, 54.6, 52.7, 50.8, 47.9, 47.7, 36.0, 16.0; IR ($CHCl_3$, cm^{-1}) 3017, 1216; HRMS calcd for $C_{12}H_{18}O_3$ 210.1246, found 210.1244.

To a stirred solution of 5.0 g (23.8 mmol) of epoxy acetal in 5 mL of 1,4-dioxane was added 6 mL of 28% aqueous ammonia solution. The mixture was heated in a sealed tube at 120 °C for 6 h to afford the corresponding β-amino alcohol. After the solvent was removed, the residue was diluted with 30 mL of water. The solution was cooled to 0 °C, 1.6 mL (30.7 mmol) of acetic acid was added with stirring, and a solution of 2.12 g (30.7 mmol) of sodium nitrite in 20 mL of water was added over a period of 4 h. Stirring was continued at 0 °C for 2 h and then for an additional 4 h with no further external cooling. The reaction mixture was neutralized with a cold saturated aqueous solution of sodium bicarbonate. The product was extracted with ethyl acetate (90 × 4 mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$), filtered, and evaporated *in vacuo* to afford crude **6.** Chromatography on silica gel (elution with 4:1 *n*-hexane/ethyl acetate) afforded 3.8 g (76%) of bicyclo[3.2.1]ketone **6** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29 (dd, J = 6.0, 3.0 Hz, 1H), 6.10 (dd, J = 6.0, 3.0 Hz, 1H), 4.36 (d, J = 9.0 Hz, 1H), 3.36 (s, 6H), 2.98 (dd, J = 4.8, 3.0 Hz, 1H), 2.86−2.79 (m, 1H), 2.67−2.63 (m, 1H), 2.27−2.22 (m, 3H), 0.93 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 136.9, 133.7, 102.8, 56.1, 54.7, 54.4, 52.7, 45.2, 43.5, 27.4, 19.5; IR ($CHCl_3$, cm^{-1}) 2937, 1708; HRMS calcd for $C_{12}H_{18}O_3$ 210.1246, found 210.1244.

***endo*-4-Methyl-*syn*-8-(dimethoxymethyl)-3-(methylthio)-bicyclo[3.2.1]oct-6-en-2-one (9)**. A solution of ketone **6** (2.0 g, 9.5 mmol) in benzene, 20 mL containing 0.45 g (19.1 mmol) of sodium hydride, and 1.34 mL (14.3 mmol) of dimethyl disulfide was refluxed for 12 h. The reaction mixture was treated with water (20 mL) and extracted with ethyl acetate (20 × 3 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to produce crude **9**. Chromatography on silica gel (elution with 6:1 *n*-hexane/ethyl acetate) afforded 1.7 g (70%) of ketosulfide **9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 (dd, J = 5.7, 2.7 Hz, 1H), 6.15 (dd, J = 5.7, 3.3 Hz, 1H), 4.32 (d, J = 8.4 Hz, 1H), 3.38 (s, 3H), 3.35 (s, 3H), 3.17−3.15 (m, 1H), 3.08 (d, J = 9.3 Hz, 1H), 2.79−2.72 (m, 2H), 2.23 (s, 3H), 2.05−1.95 (m, 1H), 1.18 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.9, 137.3, 133.8, 102.5, 57.6, 56.6, 55.2, 54.8, 52.9, 45.9, 35.0, 18.6, 16.5; IR ($CHCl_3$, cm^{-1}) 2971, 2926, 1750; HRMS calcd for $C_{13}H_{20}O_3S$ 256.1130, found 256.1127.

***endo*-9-Methyl-8-hydroxy-1-(methylthio)tricyclo-[4.2.1.0^{3,7}]non-4-en-2-one (10).** To 2.0 g (7.8 mmol) of keto-sulfide **9** were added 10 mL of acetone and 10 mL of 2 N hydrochloric acid. The reaction mixture was heated at reflux for 4 h, after which time it was cooled 25 °C and neutralized with a cool solution of sodium bicarbonate. The product was isolated with ethyl acetate extraction (30 × 3 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to produce crude **10**. Chromatography on silica gel (elution with 4:1 *n*-hexane/ethyl acetate) afforded 1.4 g (85%) of the β-hydroxy keto sulfide **10** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.07−5.98 (m, 2H), 4.22 (s, brs, 1H), 3.43−3.40 (m, 1H), 3.22−3.18 (m, 1H), 2.96−2.94 (m, 1H), 2.87−2.80 (m, 1H), 2.10 (brs, 1H), 2.02 (s, 3H), 0.83 (d, J = 7.2 Hz, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.6, 138.7, 130.5, 75.0, 72.6, 57.2, 55.2, 45.7, 42.9, 11.6, 11.2; IR ($CHCl_3$, cm^{-1}) 1741, 1101; HRMS calcd for $C_{11}H_{14}O_2S$ 210.0715, found 210.0714.

***endo*-9-Methyl-8-[(methylsulfonyl)oxy]-1-(methylthio)-tricyclo[4.2.1.0^{3,7}]non-4-en-2-one (5).** Methanesulfonyl chloride (1.1 mL, 9.5 mmol) was added dropwise to a cold (0 °C), magnetically stirred solution of **10** (1.0 g, 4.8 mmol) in pyridine (10 mL). After being allowed to warm to 25 °C, the mixture was stirred for 2 h. Water (10 mL) was then added to the mixture and the resulting solution extracted with ethyl acetate (30 × 3 mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$), filtered, and concentrated to produce crude **5**. Chromatography on silica gel (elution with 6:1 *n*-hexane/ethyl acetate) afforded 1.2 g (88%) of the mesylate **5** as a colorless solid that was recrystallized from hexane−ethyl acetate (50:50): mp = 152−154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.07−6.00 (m, 2H), 5.13 (s, brs, 1H), 3.60−3.56 (m, 1H), 3.30−3.23 (m, 1H), 3.23 (s, 3H), 3.09−3.06 (m, 1H), 2.88−2.83 (m, 1H), 2.07 (s, 3H), 0.84 (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 138.2, 130.6, 81.0, 73.1, 57.4, 54.6, 45.7, 43.0, 39.3, 11.7, 11.0; IR ($CHCl_3$, cm^{-1}) 1748, 1172; HRMS calcd for $C_{12}H_{16}O_4S_2$ 288.0491, found 288.0644. Anal. Calcd for $C_{12}H_{16}O_4S_2$: C, 49.98; H, 5.59. Found: C, 50.15; H, 5.59.

***endo*-2-(Methoxycarbonyl)-*endo*-6-methyl-7-(methylthio)-*cis*-bicyclo[3.3.0]octa-3,7-diene (13).** To mesylate **5** (1.0 g, 3.5 mmol) were added tetrahydrofuran (10 mL), water (10 mL), and potassium hydroxide (0.5 g, 8.9 mmol). The reaction mixture was heated at reflux for 5 h. It was then cooled to room temperature, and the aqueous layer was collected. The aqueous layer was acidified with 2 N hydrochloric acid and extracted with ether (20 × 3 mL). The combined organic extracts were washed with brine and water, dried ($MgSO_4$), and concentrated to afford crude acid. Acid was dissolved in diethyl ether and treated with diazomethane. After 15 min, nitrogen was bubbled into the solution to remove excess diazomethane. The ether solution was concentrated, and chromatography on silica gel (elution with 9:1 *n*-hexane/ethyl acetate) afforded vinylsulfide ester **13** (0.54 g, 70%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85−5.81 (m, 1H), 5.75−5.72 (m, 1H), 3.81−3.77 (m, 1H), 3.71 (s, 3H), 3.61−3.58 (m, 1H), 3.31−3.23 (m, 1H), 2.73−2.64 (m, 1H), 2.26−2.19 (m, 1H), 2.17 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 136.8, 132.5, 128.0, 127.2, 62.5, 53.6, 51.5, 40.4, 38.5, 14.7, 13.9; IR ($CHCl_3$, cm^{-1}) 1728, 1195; HRMS calcd for $C_{12}H_{16}O_2S$ 224.0872, found 224.0871.

***endo*-2-(Methoxycarbonyl)-*endo*-6-methyl-*cis*-bicyclo-[3.3.0]oct-3-en-7-one (14).** A solution of ester **13** (0.5 g, 2.2 mmol) in acetonitrile (9 mL) containing water (3 mL) and mercury(II) chloride (1.5 g, 5.6 mmol) was refluxed for 4 h. The reaction mixture was treated with water (10 mL) and extracted with ethyl acetate (30 × 3 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated to produce the crude keto ester. Chromatography on silica gel (elution with 9:1 *n*-hexane/ethyl

acetate) afforded the keto ester (0.3 g, 70%) as a mixture of diastereomers (*endo*-**14**:*exo*-**15** = 1.3:1).

14: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91−5.88 (m, 1H), 5.84−5.81 (m, 1H), 3.83−3.79 (m, 1H), 3.68 (s, 3H), 3.31−3.20 (m, 1H), 3.04−2.99 (m, 1H), 2.36 (dd, J = 18.6, 9.6 Hz, 1H), 2.31−2.29 (m, 1H), 2.14 (dd, J = 18.6, 5.4 Hz, 1H), 1.15 (d, J = 5.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.0, 173.1, 136.2, 128.7, 55.0, 53.9, 51.7, 47.4, 39.4, 38.5, 16.0; IR ($CHCl_3$, cm^{-1}) 1731, 1427; HRMS calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0944.

15: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92−5.88 (m, 1H), 5.83−5.78 (m, 1H), 3.86−3.84 (m, 1H), 3.66 (s, 3H), 3.54−3.44 (m, 1H), 3.30−3.18 (m, 1H), 2.52−2.32 (m, 2H), 1.92 (m, 1H), 1.11 (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.6, 172.9, 131.6, 130.0, 54.3, 52.0, 51.7, 46.6, 38.8, 38.3, 11.0.

***endo*-7-(Methoxycarbonyl)-*endo*-2-methyl-3-oxa-*cis*-bicyclo[4.3.0]non-8-en-4-one (16).** To a solution of keto ester **14** (250 mg, 1.3 mmol) in 30 mL of methylene chloride was added 161 mg of sodium bicarbonate followed by 242 mg (1.4 mmol) of purified *m*-chloroperbenzoic acid. After being stirred at room temperature for 12 h, the reaction mixture was extracted with saturated aqueous sodium bicarbonate solution. Chromatography on silica gel (elution with 1:1 *n*-hexane/ethyl acetate) afforded 203 mg (75%) of the lactone **16** as a colorless solid, which was recrystallized from hexane−ethyl acetate (80:20): mp = 39−41 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88−5.85 (m, 1H), 5.74−5.72 (m, 1H), 4.14−4.05 (m, 1H), 3.90−3.85 (m, 1H), 3.72 (s, 3H), 3.14−3.01 (m, 1H), 2.94−2.86 (m, 1H), 2.47 (dd, J = 14.4, 6.0 Hz, 1H), 2.37 (t, J = 14.4 Hz, 1H), 1.45 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 172.7, 131.3, 131.1, 77.0, 53.6, 52.4, 52.0, 35.3, 30.7, 19.3; IR ($CHCl_3$, cm^{-1}) 1734, 1172; HRMS calcd for $C_{11}H_{14}O_4$ 210.0892, found 210.0893.

(±)-Sarracenin (1). To a solution of 150 mg (0.7 mmol) of lactone **16** in 10 mL of THF was added rapidly and with stirring at −78 °C 1.5 mL (1.4 mmol) of a 1 M solution of diisobutylaluminum hydride in hexane. After 1.5 h, 1.0 mL of dry methanol, precooled to −78 °C, was added. After 20 min, the reaction was warmed slowly to 0 °C and then partitioned between water and ethyl acetate. The organic extracts were washed twice with a saturated, aqueous sodium bicarbonate solution and then concentrated, leaving 106 mg (70%) of crude lactol, used without further purification. A solution of 106 mg (0.5 mmol) of crude lactol in 15 mL of methylene chloride was ozonized with excess ozone in oxygen at −78 °C. After removal of the solvent the oily residure was dissolved in 6 mL of glacial acetic acid, and excess zinc dust was added. After being stirred at 25 °C for 80 min, the mixture was filtered through a layer of cotton and then heated at 70 °C for 80 min. The solvent was removed under high vaccum to give 80 mg of an oil. Chromatography on silica gel (elution with 3:1 *n*-hexane/ethyl acetate) afforded 45 mg of sarracenin (27%) as a needleless solid: mp = 107−108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 1H), 5.79 (d, J = 1.8 Hz, 1H), 4.99 (d, J = 3.3 Hz, 1H), 4.21 (d, J = 6.5 Hz, 1H), 3.75 (s, 3H), 3.00−2.95 (m, 1H), 2.41−2.33 (m, 1H), 1.70−1.64 (m, 2H), 1.35 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 150.1, 112.3, 91.7, 88.1, 69.0, 51.4, 35.1, 32.2, 22.0, 18.7; HRMS calcd for $C_{11}H_{14}O_5$ 226.0841, found 226.0845. Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.24; H, 5.92.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR and ORTEP diagrams for **5** and **16** (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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