solution of 1.04 g (3.95 mmol) of **6b** and 99 mg (0.40 mmol) of pyridinium *p*-toluenesulfonate in 3.80 mL (2.86 g, 39.7 mmol) of ethyl vinyl ether and 20 mL of CH_2Cl_2 under argon was stirred at room temperature for 4 h. One drop of pyridine was added to the reaction mixture, which was then processed with CH_2Cl_2 in the usual way. The crude product was purified by silica gel chromatography with 20% ether in hexane to provide 1.19 g (90%) of 1,1-dimethylethyl (*N*-((1*S*,2*S*)-2-(1-ethoxyethoxy)-1-phenyl-3-butenyl)amino)methanoate: mp 59–65 °C; $[\alpha]^{25}_D$ +15° (*c* 1.6, $CHCl_3$); ^1H NMR (300 MHz) δ 7.37–7.17 (m, 5 H), 5.91 and 5.77 (2ddd, *J* = 7, 10.5, 17.4 Hz, 1 H), 5.44 and 5.37 (2m, 1 H), 5.30 and 5.25 (2dt, *J* = 1.2, 17.4 Hz, 1 H), 5.23 and 5.22 (2dt, *J* = 1.2, 10.5 Hz, 1 H), 4.73 and 4.71 (2m, 1 H), 4.62 and 4.31 (2q, *J* = 5.4 and 5.3 Hz, 1 H), 4.23 and 4.16 (2 pseudo dd, *J* = 6.6, 7.0 Hz, 1 H), 3.51–3.05 and 2.98–2.90 (2 m, 2 H), 1.40 (s, 9 H), 1.22 and 1.05 (2d, *J* = 5.4 and 5.3 Hz, 3 H), 1.07 and 0.90 (2t, *J* = 7.0 Hz, 3 H); IR 3370, 1680, 1520, 1170, 1080, 1050 cm^{-1}. Anal. Calcd for $C_{19}H_{29}O_4N$: C, 68.03; H, 8.71; N, 4.18. Found: C, 68.00; H, 8.78; N, 4.13.

The above acetal (1.09 g, 3.25 mmol) was treated as was that from **6a** to afford 940 mg (82%) of pure **1b**: mp 33–37 °C; $[\alpha]^{25}_D$ +18° (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz) δ 8.52 (br s, 1 H), 7.38–7.13 (m, 5 H), 5.72 (br s, 1 H), 5.29 (br s, 1 H), 4.80–4.65 and 4.50–4.35 (2m, 2 H), 3.52–3.15 and 2.88–2.60 (2m, 2 H), 1.42 (s, 9 H), 1.20 and 1.18 (2d, *J* = 5.4 Hz, 3 H), 1.04 and 0.81 (2t, *J* = 7.0 Hz, 3 H); IR 3700–2200, 3060, 1720, 1660, 1370, 1170, 1080, 955 cm^{-1}. The methyl ester of **1b** (CH_2N_2) was identical with material previously prepared by an alternative synthesis.[5b] ^1H and ^{19}F NMR analysis of the Mosher esters of the alcohols derived from the methyl esters of (±)-**1b** and (+)-**1b** (aqueous HCl; (*R*)-(−)-2-methoxy-2-phenyl-2-trifluoromethylacetyl chloride, pyridine) confirmed the enantiomeric purity (≥99%) of (+)-**1b**.

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Registry No. **1a** (isomer 1), 136778-67-1; **1a** (isomer 2), 136778-69-3; **1a** (methyl ester; isomer 1), 136779-75-4; **1a** (methyl ester; isomer 2), 136778-73-9; **1a** (methyl ester; Mosher ester), 136693-08-8; **1b** (isomer 1), 136778-68-2; **1b** (isomer 2), 136778-70-6; **1b** (methyl ester; isomer 1), 136778-71-7; **1b** (methyl ester; isomer 2), 136778-75-1; **1b** (methyl ester; Mosher ester), 136693-09-9; **2**, 32981-86-5; **3a**, 33069-62-4; **3b**, 114977-28-5; **4**, 2935-35-5; **5a**, 116126-04-6; **5b**, 117049-14-6; **6a**, 136693-02-2; *anti*-**6a**, 136693-06-6; **6a** ((*R*)-ethoxyethyl ether), 136693-04-4; **6a** ((*S*)-ethoxyethyl ether), 136778-72-8; **6b**, 136693-03-3; *anti*-**6b**, 136693-07-7; **6b** ((*R*)-ethoxyethyl ether), 136778-74-0; **6b** ((*S*)-ethoxyethyl ether), 136693-05-5.

Singlet Oxygen Mediated Oxidative Decarboxylation of Pyrrole-2-carboxylic Acids

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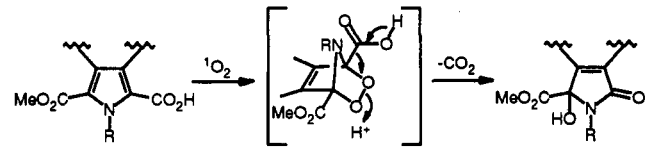
Autoxidation of the chromogen hermidin[1] isolated from *Mercurialis perennis L.*[2] provides isochrysohermidin (1),[3] a functionalized 3,3′-pyrrolin-2-one dimer first isolated from *Mercurialis leiocarpia* and whose structure was unambiguously established by X-ray crystallography. In initial studies directed at the total synthesis of isochrysohermidin,[4] we have examined the singlet oxygen ($^1O_2$) addition[5] to substituted 5-(alkoxycarbonyl)pyrrole-2-carboxylic acids and a subsequent oxidative decarboxylation[6] reaction in efforts to provide direct access to the 5-(alkoxycarbonyl)-5-hydroxy-3-pyrrolin-2-one subunit found in **1**, Scheme I.

Scheme I



Scheme II

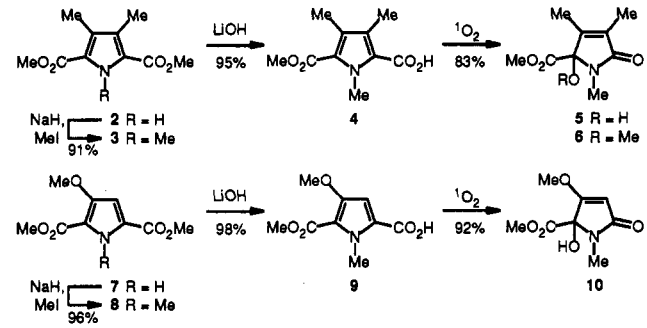
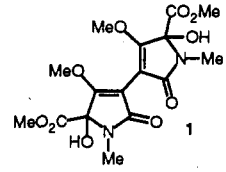


Table I

pyrrole	solvent (0.8 mM)[a]	time (h)	result
4	CH_3OH[b]	5	**5** (20%), **6** (12%)
	CH_3OH	1	**5** (35%), **6** (32%)
	CH_3OH–H_2O (2:1)	1	**5** (37%), **6** (26%)
	^iPrOH–H_2O (2:1)	1	**5** (79%)
	^iPrOH–H_2O (3:1)	1	**5** (83%)
	CH_3CN–H_2O (3:1)	1	**5** (62%)
9	CH_3CN–H_2O (3:1)	1	**10** (92%)
	^iPrOH–H_2O (3:1)	1	**10** (80%)

[a] Rose bengal (8 mequiv), quartz immersion well, Hanovia high-pressure mercury lamp (450 W), uranium yellow glass filter (transmits > 330 nm), O_2, 22 °C. [b] Pyrex reaction vessel, tungsten lamp (500 W), O_2, 22 °C.



1

The substrates employed in the study were derived from the [4 + 2] cycloaddition of 2-[(triethylsilyl)oxy]-2-butene and 1,1-dimethoxyethylene with 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine[7] followed by reductive ring contraction (Zn, HOAc) of the resulting 1,2-diazine cycloadducts to provide the substituted pyrroles **2** and **7**.[8] *N*-Methylation of the pyrroles followed by a surprisingly selective monohydrolysis of the symmetrical pyrrole **3** and a well-precedented[9] selective hydrolysis of the sterically

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and electronically more accessible methoxycarbonyl group of the unsymmetrical pyrrole 8 provided the carboxylic acids 4 (95%) and 9 (98%) in excellent yields, Scheme II.

A survey of reaction conditions conducted with 4 revealed that the $^1O_2$ addition to the pyrrole was most effectively conducted in a quartz immersion well equipped with a uranium yellow glass filter (transmits > 330 nm) employing a high-pressure Hanovia mercury lamp (450 W) in the presence of rose bengal (8 mequiv). The subsequent oxidative decarboxylation reaction was found to proceed at room temperature to provide 5 directly, Table I. Reactions conducted with methanol[6] as solvent or cosolvent led to the generation of 6[10] and the competitive hemiaminal exchange with solvent was eliminated through the use of 2-propanol or acetonitrile as the cosolvent for the reaction. Under optimized reaction conditions, the treatment of 4 with $^1O_2$ provided 5 in 83% yield.

The extension of the observations to 9 possessing the pyrrole functionality found in isochrysohermidin confirmed the generality of the reaction and verify its potential application within a projected total synthesis of isochrysohermidin. Treatment of 9 with $^1O_2$ under the prescribed reaction conditions provided 10 directly in 92% yield, Table I.

The extension of these observations in a total synthesis of isochrysohermidin are in progress and will be reported in due course.

Experimental Section[11]

Dimethyl 1,3,4-Trimethylpyrrole-2,5-dicarboxylic Acid (3). A suspension of NaH (57 mg, 1.42 mmol, 1.5 equiv, washed free of oil with 3 × 2 mL of pentane) in DMF (4.0 mL, 0.24 M) was cooled to −10 °C, treated dropwise with a solution of 2,5-bis(methoxycarbonyl)-3,4-dimethylpyrrole[8] (2, 200 mg, 0.95 mmol) in DMF (4.0 mL), and the reaction solution was allowed to warm to 22 °C over 2 h. The reaction mixture was recooled to −10 °C, treated dropwise with methyl iodide (673 mg, 4.74 mmol, 5.0 equiv), and allowed to warm to 22 °C over 12 h. The mixture was partitioned between Et_2O and H_2O. The ether layer was dried (Na_2SO_4) and concentrated under reduced pressure to afford 220 mg of a crude yellow solid. Recrystallization from Et_2O/hexane afforded 3 as a white solid (193 mg, 213 mg theoretical, 91%): mp 107–108 °C (white needles); ^1H NMR ($CDCl_3$, 200 MHz) δ 4.09 (s, 3 H, N-Me), 3.88 (s, 6 H, CO_2Me), 2.20 (s, 6 H, Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 162.7 (e, CO_2Me), 126.6 (e, C-2), 125.2 (e, C-3), 51.2 (o, CO_2Me), 35.0 (o, N-Me), 10.8 (o, Me); UV ($CHCl_3$) λ_{max} 288 nm (ε 17000); IR (KBr) ν_{max} 3054, 2987, 1718, 1701, 1697, 1560, 1540, 1266, 1141, 896 cm^{-1}; EIMS *m/e* (relative intensity) 225 (M^+, base), 210 (29), 194 (45), 166 (18), 150 (22); CIMS (isobutane) *m/e* 226 (M + H^+, base); EIHRMS *m/e* 225.1001 ($C_{11}H_{15}NO_4$ requires 225.1001).

Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.51; H, 6.68; N, 6.16.

2-Carboxy-5-(methoxycarbonyl)-1,3,4-trimethylpyrrole (4). A solution of 3 (45 mg, 0.20 mmol) in 2:1 methanol–water (3.75 mL, 0.06 M) was treated with lithium hydroxide (11 mg, 0.26 mmol, 1.3 equiv) and allowed to stir at 22 °C under nitrogen. After 80 h, the reaction mixture was partitioned between Et_2O and H_2O. The aqueous layer was acidified (pH 1) with the addition of 10% aqueous HCl and extracted with CH_2Cl_2 (5 × 10 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford 45 mg of a crude yellow solid. Recrystallization (^{i}PrOH) afforded 4 as a pure white solid (40 mg, 42 mg theoretical, 95%): mp 175–176 °C (white solid, dec); ^1H NMR ($CDCl_3$, 200 MHz) δ 4.12 (s, 3 H, N-Me), 3.89 (s, 3 H, CO_2Me), 2.27 (S, 3 H, Me), 2.21 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167.4 (e, CO_2H), 162.6 (e, CO_2Me), 129.3 (e, C-2), 126.5 (e, C-5), 123.8 (e, C-4), 118.5 (e, C-3), 51.3 (o, CO_2Me), 35.2 (o, N-Me), 11.0 (o, Me), 10.7 (o, Me); UV ($CHCl_3$) λ_{max} 284 nm (ε 14600); IR (KBr) ν_{max} 3439, 2917, 2849, 1718, 1670, 1437, 1282 cm^{-1}; EIMS *m/e* (relative intensity) 211 (M^+, base), 180 (27), 166 (12), 152 (12), 151 (11), 148 (14), 65 (12), 57 (15); CIMS (isobutane) *m/e* 212 (M + H^+, base); EIHRMS *m/e* 211.0845 ($C_{10}H_{13}NO_4$ requires 211.0845).

Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.47; H, 6.20; N, 6.98.

5-Hydroxy-5-(methoxycarbonyl)-1,3,4-trimethyl-3-pyrrolin-2-one (5). A solution of 4 (26 mg, 0.12 mmol) in 3:1 isopropyl alcohol–water (150 mL, 0.8 mM) was treated with rose bengal (980 μg, 8 mequiv), and the solution was irradiated in a Quartz immersion vessel with a Hanovia high-pressure mercury lamp (450 W) through a uranium yellow glass filter (transmits > 330 nm) with a steady stream of oxygen bubbling through the solution at 22 °C. After 1 h, the reaction mixture was extracted with CH_2Cl_2 (5 × 100 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography (SiO_2, 1 cm × 10 cm, Et_2O) afforded 5 as a colorless oil (20 mg, 24 mg theoretical, 83%): ^1H NMR ($CDCl_3$, 500 MHz) δ 4.23 (bs, 1 H, OH), 3.82 (s, 3 H, CO_2Me), 2.79 (s, 3 H, N-Me), 1.83 (s, 6 H, two Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.8 (e, CO_2Me), 171.7 (e, C=O), 146.5 (e, C-4), 131.4 (e, C-3), 89.6 (e, C-5), 54.0 (o, CO_2Me), 24.0 (o, N-Me), 9.5 (o, C-4 Me), 8.5 (o, C-3 Me); UV ($CHCl_3$) λ_{max} 250 nm (ε 875); IR (neat) ν_{max} 3285, 2957, 2925, 1749, 1694, 1438, 1249, 1101 cm^{-1}; EIMS *m/e* (relative intensity) 199 (M^+, 1), 140 (base), 59 (55), 58 (37), 55 (20), 54 (12); CIMS (isobutane) *m/e* 200 (M + H^+, base); CIHRMS *m/e* 200.0923 ($C_9H_{13}NO_4$ requires 200.0923).

Dimethyl 3-Methoxy-1-methylpyrrole-2,5-dicarboxylic Acid (8). A suspension of NaH (130 mg, 3.24 mmol, 1.3 equiv, washed free of oil with 3 × 5 mL of pentane) in DMF (4.0 mL, 0.25 M) was cooled to −10 °C and treated dropwise with a solution of dimethyl 3-methoxypyrrole-2,5-dicarboxylic acid[9] (7, 530 mg, 2.48 mmol) in DMF (6.0 mL), and the reaction was allowed to warm to 22 °C over 2 h. The reaction mixture was recooled to −10 °C, treated dropwise with methyl iodide (1.77 g, 12.5 mmol, 5.0 equiv), and allowed to warm to 22 °C over 12 h. The mixture was partitioned between Et_2O and H_2O. The ether layer was dried (Na_2SO_4) and concentrated under reduced pressure to afford 600 mg of a crude yellow solid. Chromatography (SiO_2, 3 cm × 10 cm, Et_2O) afforded 8 as a white solid (540 mg, 565 mg theoretical, 96%): mp 97–99 °C (^{i}PrOH, colorless needles); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.38 (s, 1 H, C-4 CH), 4.06 (s, 3 H, N-Me), 3.75 (s, 3 H, OMe), 3.72 (s, 6 H, CO_2Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 161.2 (e, C-5 CO_2Me), 160.6 (e, C-2, CO_2Me), 152.0 (e, C-3), 124.2 (e, C-5), 113.4 (e, C-2), 100.1 (o, C-4), 57.3 (o, OMe), 51.0 (o, CO_2Me), 50.8 (o, CO_2Me), 33.9 (o, N-Me); UV ($CHCl_3$) λ_{max} 286 nm (ε 10100); IR (KBr) ν_{max} 3142, 2951, 1721, 1692, 1554, 1496, 1482, 1441, 1419, 1234, 1159, 1110, 1091, 775 cm^{-1}; EIMS *m/e* (relative intensity) 227 (M^+, base), 212 (16), 196 (46), 194 (21), 180 (51), 53 (15); CIMS (isobutane) 228 (M + H^+, base); EIHRMS *m/e* 227.0790 ($C_{10}H_{13}NO_5$ requires 227.0794).

Anal. Calcd for $C_{10}H_{13}NO_5$: C, 52.86; H, 5.77; N, 6.16. Found: C, 52.87; H, 5.89; N, 6.35.

2-Carboxy-4-methoxy-5-(methoxycarbonyl)-1-methylpyrrole (9). A solution of 8 (90 mg, 0.40 mmol) in 3:1:1 THF–methanol–water (1.6 mL, 0.25 M) was treated with lithium hydroxide (17 mg, 0.40 mmol, 1.0 equiv) and allowed to stir at 22 °C under nitrogen. After 78 h, the reaction mixture was partitioned between Et_2O and H_2O. The aqueous layer was acidified (pH 1) with the addition of 10% aqueous HCl and extracted with EtOAc (5 × 15 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford 90 mg of a crude yellow solid. Recrystallization (^{i}PrOH) afforded 9 as a colorless solid (83 mg, 85 mg theoretical, 98%): mp 212–214 °C dec (colorless plates); ^1H NMR (CD_3COCD_3, 300 MHz) δ 10.80 (bs, 1 H, CO_2H), 6.62 (s, 1 H, C-3 CH), 4.15 (s, 3 H, N-Me), 3.81 (s, 3 H, OMe), 3.79 (s, 3 H, CO_2Me); ^{13}C NMR (CD_3COCD_3, 50 MHz) δ 159.4 (e, CO_2H), 159.3 (e, CO_2Me), 150.5 (e, C-4), 122.9 (e, C-2), 105.2 (e, C-5), 99.0 (o, C-3), 55.2 (o, OMe), 48.3 (o, CO_2Me), 31.6 (o, N-Me); UV (EtOAc) λ_{max} 282 nm (ε 10930); IR (KBr) ν_{max} 3676, 3429, 3133, 2961, 1707, 1664, 1552, 1423, 1246, 1188, 1118, 731 cm^{-1}; EIMS

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(10) For 6: ^1H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, 3 H, CO_2Me), 3.02 (s, 3 H, OMe), 2.81 (s, 3 H, NMe), 1.88 (s, 3 H, Me), 1.85 (s, 3 H, Me); IR (neat) ν_{max} 2956, 1748, 1700, 1438, 1374, 1258, 1106, 1054 cm^{-1}; EIMS *m/e* (relative intensity) 213 (M^+, 0.4), 154 (base), 140 (14), 49 (10); CIMS (isobutane) *m/e* 214 (M + H^+, base); CIHRMS *m/e* 214.1075 ($C_{10}H_{15}NO_4$ requires 214.1079).

(11) For ^{13}C NMR, the notation (e) for even and (o) for odd refer to the number of attached protons established by APT ^{13}C NMR.

m/e (relative intensity) 213 (M^+, base), 198 (15), 182 (39), 180 (31), 166 (61), 66 (18), 53 (19); CIMS (isobutane) m/e 214 ($M + H^+$, base); EIHRMS m/e 213.0635 ($C_9H_{11}NO_5$ requires 213.0637).

5-Hydroxy-4-methoxy-5-(methoxycarbonyl)-1-methyl-3-pyrrolin-2-one (10). A solution of **9** (64 mg, 0.30 mmol) in 3:1 acetonitrile–water (376 mL, 0.8 mM) was treated with rose bengal (2.4 mg, 8 mequiv) and the solution was irradiated in a Quartz immersion vessel with a Hanovia high-pressure mercury lamp (450 watts) through a uranium yellow glass filter (transmits >330 nm) with a steady stream of oxygen bubbled through the solution at 22 °C. After 1 h, the reaction mixture was extracted with CH_2Cl_2 (5 × 100 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford 74 mg of an orange oil. Chromatography (SiO_2, 2 cm × 15 cm, Et_2O) afforded **10** as a colorless oil (55 mg, 60 mg theoretical, 92%): ^1H NMR ($CDCl_3$, 300 MHz) δ 5.11 (s, 1 H, C-3 CH), 4.52 (s, 1 H, OH), 3.87 (s, 3 H, OMe), 3.84 (s, 3 H, CO_2Me), 2.74 (s, 3 H, N-Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 172.0 (e, CO_2Me), 170.8 (e, C=O), 169.8 (e, C-4), 94.2 (o, C-3), 87.1 (e, C-5), 58.7 (o, OMe), 54.2 (o, CO_2Me), 23.4 (o, N-Me); UV (EtOAc) λ_{max} 262 nm (ϵ 960); IR (neat) ν_{max} 3421, 3133, 2958, 1762, 1685, 1647, 1434, 1234, 1136, 1043 cm^{-1}; EIMS m/e (relative intensity) 201 (M^+, 2), 142 (base), 82 (16), 69 (16), 57 (11); CIMS (isobutane) m/e 202 ($M + H^+$, base); EIHRMS m/e 201.0639 ($C_8H_{11}NO_5$ requires 201.0637).

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Registry No. 1, 104006-84-0; 2, 78331-70-1; 3, 136629-78-2; 4, 136629-79-3; 5, 136629-80-6; 6, 136629-81-7; 7, 92144-13-3; 8, 136629-82-8; 9, 136629-83-9; 10, 136629-84-0; lithium hydroxide, 1310-65-2; oxygen, 7782-44-7; rose bengal, 11121-48-5.

Supplementary Material Available: ^1H NMR of 3–6, 8–10 is provided (7 pages). Ordering information is given on any current masthead page.

Peroxidation of Saccharide Phenylhydrazones: Novel Hydrazono-1,4-lactones

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It is known[1-5] that phenylhydrazones undergo autoxidation by free-radical mechanisms to afford phenylazo hydroperoxides. The reaction is usually carried out at room temperature by shaking a solution of the hydrazone in benzene with oxygen or air. It is also known[6] that saccharide phenylhydrazones kept in contact with oxygen in the presence of bases produce free radicals detectable by ESR. We have now isolated stable products produced from these free radicals and found them to be novel hydrazono-1,4-lactones (**4a–c**).

Solutions of the phenylhydrazones of D-galactose (**1a**), 6-deoxy-D-galactose (D-fucose) (**1b**), and D-arabinose (**1c**) and their L enantiomers in aqueous ethanol containing enough KOH to bring the pH to 12–14 were stirred at room temperature in the presence of air. *Warning: Bubbling air or oxygen in such solutions leads to spontaneous explosion of dry peroxides formed on the reaction vessel walls.* In each case, analysis by HPLC showed a gradual decrease in the amount of starting hydrazone and the formation of a new product. Combustion analysis and EI–MS agreed with formulas having two hydrogen atoms less than the starting hydrazones. A 300-MHz proton NMR spectrum of derivative **4a** obtained from D-galactose phenylhydrazone in Me_2SO-d_6[7] showed an NH singlet, four OH protons, and a triplet and five multiplets due to aliphatic protons. The NH and OH protons were identified by ^2H_2O exchange, which altered the splitting pattern of all the C–H signals, except for a multiplet at δ 4.12. Proton decoupling also showed that this signal did not change when any of the OH protons was irradiated, denoting that its carbon was not linked to an OH group. Since the starting hydrazone possessed five hydroxyl groups, it was assumed that during the reaction one of the OH groups became involved in ring formation. Deuteration of the sample or irradiation of the lowest field OH doublet reduced a C–H triplet to a doublet, suggesting that it was generated by H-2. In order to identify the protons attached to C-3, C-4, and C-5, a COSY experiment was carried out on a deuterated sample, using the H-2 resonance to identify consecutively adjacent protons as shown in Table I. An ^1H-coupled ^{13}C NMR spectrum showed a low-field singlet (δ 150.0 ppm), which was assigned to a C=N group lacking hydrogen on the carbon and four doublets and a triplet, assigned by ^1H–^{13}C 2D NMR spectroscopy to C 2-6 as shown in Table I. To ascertain whether the product had retained its original galacto configuration or had undergone epimerization in the alkaline solution, the ^1H and ^{13}C NMR chemical shifts of the ring carbons and protons of **4a** were compared with those of D-galactono-1,4-lactone (**7d**) and of D-arabinonoimino-1,4-lactone[8] (**7e**), which has the same ring configuration as L-galactono-1,4-lactone. There was indeed a very close agreement (see Table I) in all the ^1H chemical shifts and in most of the ^{13}C resonances (one exception being C-1, which was significantly shifted to higher field upon replacement of the C=O and C=NH groups by C=NNHPh). To further confirm that product **4a** had not undergone epimerization, it was hydrolyzed with dilute acid to galactonic phenylhydrazide (**5a**). HPLC showed the absence of the enantiomeric talonic phenylhydrazide in the hydrolysate and the product was given an *N*-phenyl-D-galactonohydrazono-1,4-lactone (**4a**) structure.

The similarity between the newly prepared product **4a** and D-galactono-1,4-lactone (**7d**) is manifested by the tendency of both compounds to undergo elimination

Table I. ^1H and ^{13}C NMR Data (ppm)

^1H NMR							
compd	H-2	H-3	H-4	H-5		H-6	H-6′
7d	4.22	4.10	4.14	3.57		3.43	3.41
4a	4.35	4.05	4.12	3.61		3.56	3.51
4b	4.32	3.82	4.02	3.77		1.19 (Me)	
4c	4.34	3.98	4.19	3.73 (3.61, H-5′)			

^{13}C NMR						
compd	C-1	C-2	C-3	C-4	C-5	C-6
7d	176.1	74.5	73.7	80.9	69.8	62.9
7e	175.4	75.2	74.5	82.6	62.4	
4a	150.0	74.0	74.6	83.3	69.8	62.0[a]
4b	150.1	74.4	75.7	88.5	66.6	19.2
4c	150.6	74.3	74.8	86.3	60.8	

[a] Assignment by ^1H–^{13}C 2D NMR spectroscopy.

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