combined toluene extracts were dried over anhydrous $MgSO_4$ and the solvent was evaporated on an efficient rotary evaporator keeping the bath temperature below 40 °C. The resulting viscous oil was washed with a few milliliters of *n*-pentane to afford the sulfamyloxaziridines **1b**. The purity and diastereomer ratios were determined by NMR and melting point.

Acknowledgment. This work was supported by the National Science Foundation (CHE 8502076).

Note added in proof: We have observed that Oxone that has been exposed to moisture for several months gives reduced reactivity in the oxidations described here.

Registry No. (±)-**1a** (Z = Ph, Ar = Ph), 113548-13-3; (±)-**1a** (Z = Ph, Ar = 2-NO_2Ph), 113548-14-4; (±)-**1a** (Z = Ph, Ar = 3-NO_2Ph), 113548-15-5; (±)-**1a** (Z = Ph, Ar = 4-NO_2Ph), 113548-16-6; (±)-**1a** (Z = Ph, Ar = 2-Cl, 5-NO_2Ph), 113625-69-7; (*R*,*R*)-**1a** (Z = 10-camphoryl, Ar = 2-Cl,5-NO_2Ph), 81369-89-3; (*S*,*S*)-**1a** (Z = 10-camphoryl, Ar = 2-Cl,5-NO_2Ph), 81310-08-9; (±)-**1b** (Z = $(PhCH_2)_2N$, Ar = 2-Cl,5-NO_2Ph), 113625-70-0; (R,-*R*)-**1b** (Z = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = 3-NO_2Ph), 108167-38-0; (*S*,S)-**1b** (Z = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = 3-NO_2Ph), 108266-24-6; (*R*,*R*)-**1b** (Z = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = 2-Cl,5-NO_2Ph), 89616-61-5; (*S*,*S*)-**1b** (Z = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = 2-Cl,5-NO_2Ph), 89556-80-9; (*R*,*R*)-**1b** (Z = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = C_6F_5), 108167-42-6; (*S*,*S*)-**1b** (Z = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = C_6F_5), 108391-91-9; **2a** (Z = Ph, Ar = Ph), 13909-34-7; **2a** (Z = Ph, Ar = 2-NO_2Ph), 113567-60-5; **2a** (Z = Ph, Ar = 3-NO_2Ph), 52962-76-2; **2a** (Z = Ph, Ar = 4-NO_2Ph), 36176-89-3; **2a** (Z = Ph, Ar = 2-Cl,5-NO_2Ph), 108167-37-9; **2b** (Z = 10-camphoryl, Ar = 2-Cl,5-NO_2Ph), 82679-82-1; **2b** (Z = $(PhCH_2)_2N$, Ar = 2-Cl,5-NO_2Ph), 108167-36-8; **2b** (*Z* = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = 2-Cl,5-NO_2Ph), 89556-76-3; **2b** (Z = (*S*)-$PhCH(CH_3)PhCH_2N$, Ar = C_6F_5), 108167-35-7; Oxone, 37222-66-5.

Conversion of Aucubin to a Useful Corey Lactone Analogue for the Synthesis of 11-Methyl PGA_2

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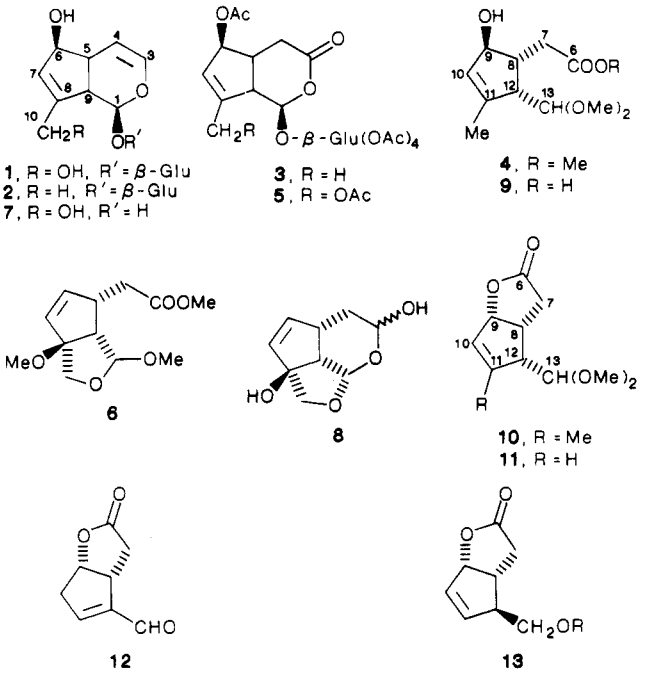
We have recently been interested in the synthesis of bioactive compounds or their intermediates from readily accessible iridoid glucosides. In particular the preparation of cyclopentenoid 1,5-dialdehydes,[1,2] of a Corey lactone analogue,[3] and, more recently, of a new 11-deoxy-11-β-methoxy-11α-(hydroxymethyl)-12-*epi*-$PGF_{2\alpha}$ methyl ester[4] from aucubin (**1**) (Chart I) have already been described.

Herein we wish to report the synthesis of bicyclic γ-lactone **10** (3-oxo-6-α-(dimethoxymethyl)-7-methyl-*cis*-2-oxabicyclo[3.3.0]7-octene),[5] a useful intermediate for 11-methyl PG's syntheses.

Our approach to **10** started from aucubin (**1**), the most diffuse and abundant iridoid glucoside[6] (20 g of **1** were

Chart I



obtained from 1 kg of fresh leaves of the common shrub *Aucuba japonica*) and represents a new route to 11-methyl PG analogues, which in some cases showed high activity.[7] In particular, 11-deoxy-11α,16,16-trimethyl PGE_2[8] (Trimoprostil), synthetized by Hoffmann La Roche Co., as well as a recent Syntex example,[9] have been successfully tested as antiulcer drugs.

Results and Discussion

Aucubin (**1**) was subjected for a short period (15 min) to a Birch reduction (Li/NH_3) at a low temperature (−90 °C). After the usual workup and chromatographic purification 10-monodeoxyaucubin (**2**) was isolated in good yield (83%) besides 6,10-dideoxyaucubin (12%).

According to the Berkowitz procedure,[10,11] the penta-*O*-acetyl derivative of **2** was transformed into the well-known acetyl lactone **3**[11] (85% overall yield from **2**), previously utilized as the 7,8-dihydro derivative for synthesis of 11-deoxy-11-methyl PG intermediates.[11]

The aim of our strategy was, on the contrary, that of retaining the Δ^7 double bond of **3** to take advantage of the reactivity of the allylic 6-OH for closure of the bicyclo γ-lactone system (Corey lactone).

Therefore, the lactone **3** was subjected to acidic methanolysis, affording, after the usual workup and final

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chromatographic purification, the dimethyl acetal methyl ester **4** (yield, 55%).

The formation of **4** from **3** was not completely predictable as, in identical conditions, the corresponding acetyl lactone **5** of aucubin underwent an acid-catalyzed rearrangement to the trimethoxy derivative **6**.[4] This transformation closely resembled the one of aucubigenin (**7**) (the aglycon of **1**) into tricyclic hemiacetal **8**.[12]

The different behavior of **3** and **5** points out the key role of allylic 10-OH in this reaction, suggesting more extensive investigation of this interesting rearrangement.

Methyl ester **4**, subjected to basic conditions was completely hydrolyzed in 8 h. The solution was acidified, and a TLC control showed the initial formation of free acid **9** and its successive complete transformation into a less polar compound, the dimethyl acetal γ-lactone **10**, which was obtained, by standard workup and chromatographic purification, as a colorless oil (84% overall yield from **4**). The α orientation of the dimethoxymethyl function at C-12 has been confirmed by a spin decoupling experiment. The irradiation of the sharp doublet at δ 4.38 (H-13) reduces the broad triplet at δ 2.97 (H-12) to a doublet with a coupling constant value ($J_{8,12}$ = 7.7 Hz) in agreement with a cis relationship between a β H-8 and H-12. The reverse trans configuration would have shown a very small J value (dihedral angle $\Phi_{8,12}$ = 90°).

The γ-lactone ring closure proceeds through an intramolecular nucleophylic attack on allylic carbocation at C-9 by the COOH group of the α-oriented side chain at C-8. An analogous tetrahydrofuran ring closure has already been described[3] for a cyclopent-10-en-9β-ol derivative (PG numbering) having a β-hydroxyethyl side chain at C-8 in the α configuration.

The Corey lactone analogue **10** (yield (**1** → **10**), 33%) can be considered a useful chiral synthon for the obtaining of 11-methyl PG's of the A, C, and F series. In fact the corresponding aldehyde **11** (11-nor derivative of **10**) resulted to be a precursor,[13] through well-known aldehyde **12**,[13] of C prostaglandins[14] and thromboxane B_2.[15] On the other hand the $\alpha \rightarrow \beta$ epimerization of the formyl group at C-12 is a routine reaction[16] in PG chemistry, and this makes **10** a potential 11-methyl derivative of **13**, a classical intermediate for PGA_2[17] and PGF[18] syntheses.

Experimental Section

General Procedures. Routine ^{1}H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32 instrument, while high-field spectra were recorded at 300 MHz on a Varian XL 300 WB. spectrometer. ^{1}H NMR data were reported as parts per million (δ) downfield from Me_4Si with the multiplicities, assignments, and J values (Hz) in parentheses. ^{13}C NMR spectra were recorded at 75 MHz on a Varian XL 300 WB. spectrometer and are reported in parts per million (ppm) downfield from Me_4Si. TLC were performed on silica gel 60 F-254 plates (E. Merck) and paper chromatography (PC) on Schleicher-Schull No. 2043 Mgl paper. Spray reagents: 2 N H_2SO_4, heating at 120 °C (TLC); vanillin [vanillin (1 g), concentrated HCl (2 mL), MeOH (100 mL)], heating at 100 °C (PC). MeOH was distilled over lithium aluminium hydride and pyridine over barium oxide.

Isolation of 1 from *Aucuba japonica*. Fresh leaves and branches of *Aucuba japonica* (2.5 kg) were roughly chopped and extracted with water (4 × 10 L) at 100 °C for 2 h, with the pH maintained in the range 7–8. A PC of the extracts [*n*-BuOH–AcOH–H_2O (63:10:27)] visualized with vanillin showed the presence of eucommiol[19] (R_f 0.51, olive-brown) as minor component and of aucubin (**1**) (R_f 0.28, pink-lilac). The aqueous extracts were concentrated in vacuo to 1 L and diluted with EtOH (4 L). The suspension was filtered, and the solution, evaporated to a small volume, was loaded onto a column of Celite, packed with water. Elution with *n*-BuOH saturated with water afforded eucommiol (4 g) and **1** (58 g), which was recrystallized from EtOH to afford 34 g of pure **1**. Chromatographic purification of the mother liquor with the same eluent gave further pure **1** (15 g): total yield of **1**, 49 g, 2%.

10-Monodeoxyaucubin (2). **1** (3 g, 8.7 mmol) was dissolved with stirring in EtOH (10 mL) and cooled at −35 °C. After the addition of liquid NH_3 (150 mL), the temperature was lowered to −90 °C, and to the stirred solution was added an excess of Li (1 g). After 20 min the deep blue solution was decolored by addition of absolute EtOH (10 mL). After 10 min both the additions (Li and EtOH) were repeated, then the mixture was allowed to stand overnight at room temperature. The residue was diluted with water (300 mL) and neutralized with 2 N HCl. Charcoal (30 g) was added to the solution with stirring, and the mixture was stratified on a gooch funnel, washed with water (5 L), and finally eluted with MeOH (600 mL). The MeOH solution was evaporated in vacuo to dryness. The residue was chromatographed on silica gel by eluting with 8:2 chloroform–methanol to afford 6,10-dideoxyaucubin (300 mg, 12%) and 10-monodeoxyaucubin (**2**) (2.4 g, 83%) as an amorphous powder: ^{1}H NMR (90 MHz, D_2O) δ 6.17 (dd, 1 H, H-3, $J_{3,4}$ = 6.3, $J_{3,5}$ = 1.8), 5.68 (br s, 1 H, H-7), 5.54 (d, 1 H, H-1, $J_{1,9}$ = 3.0), 5.05 (dd, 1 H, H-4, $J_{3,4}$ = 6.3, $J_{4,5}$ = 3.3), 4.46 (br s, 1 H, H-6), 3.19 (br s, 1 H, H-9), 2.80 (br s, 1 H, H-5), 1.88 (br s, 3 H, 3 H-10); ^{13}C NMR (D_2O) δ 146.41 (s, C-8), 139.84 (d, C-3), 128.73 (d, C-7), 106.55 (d, C-4), 95.05 (d, C-1), 81.18 (d, C-6), 49.33 (d, C-9), 41.53 (d, C-5), 15.25 (q, C-10).

Acetyl Lactone 3 from 2. See ref 11 [mp 79 °C (lit. 79–80 °C)].

Methanolysis of Lactone 3 to 4. To a stirred suspension of **3** (1 g, 1.8 mmol) in anhydrous MeOH (20 mL) was added anhydrous *p*-toluenesulfonic acid (0.3 g). The reaction mixture was stirred overnight at room temperature and then neutralized with a saturated Na_2CO_3 solution. After concentration under reduced pressure, the aqueous residue was extracted with ethyl ether (5 × 40 mL). The extracts, dried over Na_2SO_4 and evaporated in vacuo, afforded a residue, which chromatographed on silica gel [hexane–Et_2O (8:2)] gave 240 mg (yield, 55%) of pure **4** as oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (br s, 1 H, H-10), 4.22 (d, 1 H, H-13, $J_{12,13}$ = 3.3), 4.10 (br s, 1 H, H-9), 3.68 (s, 3 H, $COOCH_3$), 3.34 (s, 6 H, 2 13-OCH_3), 2.97 (br t, 1 H, H-12, $J_{12,13}$ = 3.3), 2.7–2.5 (m, 3 H, 2 H-7, H-8), 1.80 (s, 3 H, 11-CH_3); ^{13}C NMR ($CDCl_3$) δ 173.83 (s, C-6), 143.47 (s, C-11), 127.29 (d, C-10), 106.38 (d, C-13), 89.24 (d, C-9), 56.65, 55.39, 54.93 (q, 3 OCH_3), 51.34 (d, C-12), 44.18 (d, C-8), 33.47 (t, C-7), 16.91 (q, 11-CH_3).

Hydrolysis of 4: Lactone 10. To a solution of **4** (150 mg, 0.6 mmol) in MeOH (3 mL) was added a saturated solution (3 mL) of $Ba(OH)_2$ with stirring. After 8 h at room temperature the solution was extracted with Et_2O to eliminate neutral impurities and then acidified (2 N HCl) to pH 3. A TLC control [chloroform–MeOH (9:1)] showed that the free carboxylic acid **9** initially formed (R_f 0.48) was completely transformed in 2 h into the lactone **10** (R_f 0.84). After neutralization with a saturated Na_2CO_3 solution and concentration under reduced pressure, the aqueous residue was extracted with Et_2O (4 × 50 mL). The extracts, dried over Na_2SO_4 and evaporated in vacuo, afforded a residue which, chromatographed on silica gel [hexane–Et_2O (1:1)] gave pure **10** (110 mg; yield, 84%) as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (br s, 1 H, H-10), 5.32 (d, 1 H, H-9), 4.38 (d,

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1 H, H-13, $J_{12,13}$ = 6.0), 3.42 and 3.39 (s, 6 H, 2 OCH_3), 3.19 (complex m, 1 H, H-8), 2.97 (br t, 1 H, H-12, J = 7.0), 2.77 (dd, 1 H, H_{A-7}, J_{AB} = 18.0, $J_{A,8}$ = 7.2), 2.54 (dd, 1 H, H_{B-7}, J_{AB} = 18.0, $J_{B,8}$ = 10.2), 1.83 (s, 3 H, 11-CH_3); ^{13}C NMR ($CDCl_3$) δ 177.65 (s, C-6), 147.01 (s, C-11), 125.66 (d, C-10), 105.20 (d, C-13), 87.12 (d, C-9), 54.98 and 54.70 (q, 2 OCH_3), 51.58 (d, C-12), 39.01 (d, C-8), 31.02 (t, C-7), 16.07 (q, 11-CH_3).

Registry No. 1, 479-98-1; 2, 63879-67-4; 3, 86537-27-1; 4, 111795-30-3; 10, 111795-31-4; 6,10-dideoxyaucubin, 31655-27-3.

p-Benzoquinone *O*-Oxide

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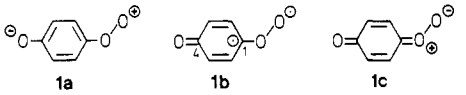
Carbonyl *O*-oxides and their isomeric dioxiranes are important intermediates in many oxidation processes.[1] Whereas some substituted dioxiranes are stable enough to be investigated in solution,[2,3] the very unstable carbonyl oxides only have lifetimes in the range of microseconds at room temperature.[4] During the last few years several carbonyl oxides have been characterized spectroscopically by using the matrix isolation technique.[5-7]

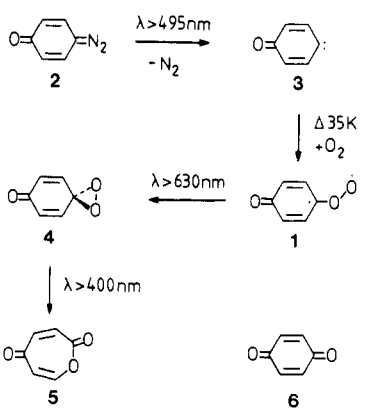
In this paper we report the matrix isolation and spectroscopic characterization of *p*-benzoquinone oxide (1). This allows for the first time a comparison of a carbonyl oxide and a carbonyl functional group in the same molecule spectroscopically. By comparison of the vibrational frequencies of both functional groups it is possible to gain information about the electronic structure of 1 and the relative importance of the resonance structures **1a–c**.[8]



1a 1b 1c

Photolysis (λ > 475 nm) of *p*-benzoquinone diazide (2),[9] matrix isolated in Ar at 9 K, gave 4-oxo-2,5-cyclohexadienylidene (3)[10] in a clean reaction (Scheme I). The

Scheme I



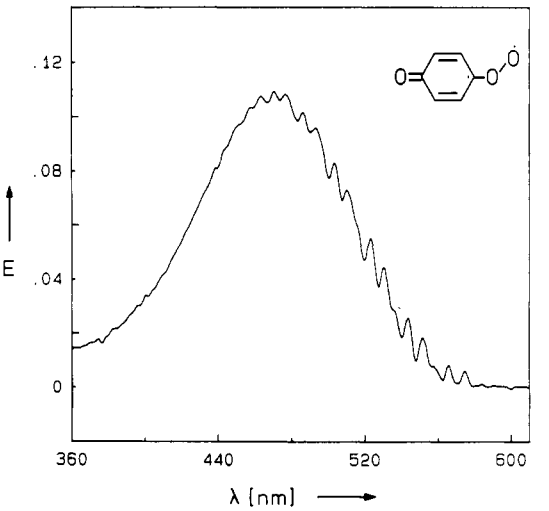


Figure 1. Vis spectrum of 1. The band is assigned to the intense $\pi \rightarrow \pi^*$ transition with λ_{max} at 462 nm.

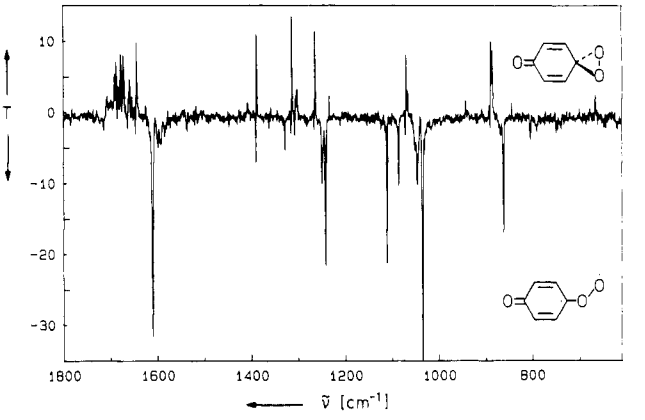


Figure 2. Difference IR spectrum showing the photochemistry of 1. Bottom: bands assigned to 1, disappearing on irradiation (λ > 630 nm). Top: new bands of 4 growing in.

IR spectrum of **3** shows an intense absorption at 1496 cm^{-1},[10] assigned to the C–O stretching mode. This vibration is found half-way between the C=O stretching mode of *p*-benzoquinone (**6**) (1682 cm^{-1})[11] and the C–O stretching mode of phenol (1250 cm^{-1}),[12] and thus a bond order of approximately 1.5 can be deduced. This finding is in agreement with ESR investigations[13] and trapping ex-

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(9) **2**: IR (Ar, 9 K) 2084 (s), 2074 (vs), 1635 (s), 1628 (s), 1591 (m), 1406 (m), 1241 (m), 1145 (m), 845 (m) cm^{-1}. **2**-d_4: IR (Ar, 9K) 2080 (vs), 2044 (m), 1630 (s), 1616 (s), 1562 (s), 1304 (s), 1140 (m), 830 (m), 745 (m), 657 (m) cm^{-1}.

(10) **3** is the primary product of the photolysis of **2**. On irradiation (λ 543 ± 20 nm) an isomer **3a** of unknown structure is formed. The photochemistry of **3** is currently under investigation. **3**: IR (Ar, 9 K) 1496 (s), 1375 (m), 1260 (m), 1076 (m), 937 (m), 819 (s) cm^{-1}; UV (Ar, 9 K) 290, 297, 338, 351, 367, 379, 496, 508, 521, 535, 550, 566 nm. **3a**: IR (Ar, 9 K) 1720 (s), 1713 (vs), 1305 (w), 1005 (m), 843 (m), 797 (m), 743 (w), 582 (s) cm^{-1}.

(11) **6**: IR (Ar, 9 K) 1707 (w), 1682 (m), 1672 (s), 1658 (m), 1596 (w), 1301 (m, δ C–H), 1066 (m, δ C–H), 942 (w), 885 (m, δ C–H). For a vibrational analysis of **6**, see: Becker, E. D.; Charney, E.; Anno, T. *J. Chem. Phys.* **1965**, *42*, 942.

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