Attempts to distill this material resulted in product decomposition, and therefore this material was converted to the ketone **18** without further purification.

4,6-Dimethoxy-2-methyl-2*H*-pyran-3(6*H*)-one (18).[17] To a solution of 6 mL of anhydrous formic acid and 2.3 mL of methanol at 20 °C was added dropwise the crude dihydrofurfuryl alcohol **17** (2.0 g, 0.010 mol) in 1.0 mL of methanol over 15 min. After an additional 10 min of stirring, the reaction was quenched into 20 mL of water and extracted with CH_2Cl_2 (5 × 20 mL). The combined organic layers were washed with saturated $NaHCO_3$ (2 × 20 mL) and brine, dried ($MgSO_4$), and concentrated to yield crude 4,6-dimethoxy-2-methyl-2*H*-pyran-3(6*H*)-one (**18**) as a tan solid: mp 56–64 °C; 1.3 g (77%). Sublimation at 31 °C (0.08 mm) yielded white needles: mp 73–74.5 °C; IR 1710 cm^{-1}; NMR ($CDCl_3$) δ 5.75 (1 H, d, 4 Hz), 5.3 (1 H, d, 4 Hz), 4.62 (1 H, q, 7 Hz), 3.68 (3 H, s), 3.52 (3 H, s), 1.3 (3 H, t, 7 Hz).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.02. Found: C, 55.55; H, 6.61. Exact mass calcd for $C_8H_{12}O_4$, 172.0735; found, 172.0731. Mass spectrum, *m/e* (relative intensity) 172 (1.9), 141 (43.8), 131 (35.1), 117 (45.2), 85 (100), 71 (24.5), 59 (23.6), 50 (64.9).

Conversion of 4,6-Dimethoxy-2-methyl-2*H*-pyran-3-(6*H*)-one (18) to Maltol. The ketone **18** (0.65 g, 0.004 mol) in 10 mL of 2 M H_2SO_4 was stirred at 25 °C for 20 min. TLC (system B, with UV visualization) showed that the ketone **18** (R_f 0.66) was cleanly converted to the γ-pyrone **1** (R = CH_3) (R_f 0.50). Isolation by adjustment to pH 2.2 and chloroform extraction yielded a light tan solid, which assayed 88% maltol by the UV assay discussed above (74% adjusted yield).

Conversion of 2-(1-Hydroxyethyl)-2,3,5-trimethoxy-2,5-dihydrofuran (17) to Maltol. The dihydrofurfuryl alcohol **17** (2.30 g, 0.012 mol) was stirred for 4 h in 50 mL of H_2SO_4 at 25 °C. TLC (system A) as above showed a high conversion of **17** to maltol. Isolation as above yielded 1.33 g of crude maltol of 78% purity (67% adjusted yield).

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Registry No. **1** (R = CH_3), 118-71-8; **1** (R = CH_2CH_3), 4940-11-8; **3** (R = CH_3), 4208-64-4; **3** (R = CH_2CH_3), 4208-61-1; **5** (R = CH_3), 41728-14-7; **6** (R = CH_3), 41728-10-3; **8** (R = CH_3, X = Br), 66187-06-2; **8** (R = CH_3, X = Cl), 66187-15-3; **9**, 3420-59-5; *cis*-**12** (R = CH_3, X = Br), 72690-03-0; *trans*-**12** (R = CH_3, X = Br), 72690-04-1; *cis*-**12** (R = CH_3, X = Cl), 72690-05-2; *trans*-**12** (R = CH_3, X = Cl), 72690-06-3; **12** (R = CH_2CH_3, X = Cl), 72622-91-4; **13** (R = CH_3, X = Br), 66187-09-5; **13** (R = CH_3, X = Cl), 66187-10-8; **13** (R = CH_2CH_3, X = Cl), 66187-11-9; **17**, 67171-01-1; **18**, 63493-69-6; 2-acetyl-2,3,5-trimethoxy-2,5-dihydrofuran, 67171-02-2.

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trans,trans-Germacra-1(10),4-dien-*cis*-6,12-olides from *Montanoa hibiscifolia*[1]

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The isolation of three germacradienolides from *Montanoa hibiscifolia* (Benth.) Sch.-Bip. is described. The deduction that these lactones, one of which has been reported previously from *M. pteropoda*, are actually members of the new class of *trans,trans*-germacra-1(10),4-dien-*cis*-6,12-olides was verified by X-ray analyses of **2a** and **4a**. Evidence is presented for the absolute configurations.

Sesquiterpene lactones have been isolated from several *Montanoa* species.[2-4] One of these is *Montanoa tomentosa* Cerv. (zoapatle) which enjoys a medicinal reputation in Mexico and also elaborates various diterpenoids, including the friedokauranolide zoapatlin[6] and the contragestationally active oxepane diterpenoids zoapatanol and montanol.[7]

Our attention was attracted to a germacradienolide recently isolated from *M. pteropoda* Blake[3] whose NMR spectrum seemed at variance with either of the proposed structures **1a** or **1b**. In particular, the small value of $J_{7,13}$ (1 Hz) suggested that the molecule might actually be **2a** or **3b** with an unprecedented (among germacradienolides) cis-lactone ring closed to C-6,[8a,b] since a heliangolide formula also capable of giving rise to such small values of $J_{7,13}$[9] was contraindicated by other data. It was also surmised that two congeners from *M. pteropoda*[3] and possibly the germacradienolide tomentosin from *M. tomentosa*[2] might possess analogous structures. We now report verification of this hypothesis for the compounds from *M. pteropoda* by isolation and structure elucidation of **2a**, **3a**, and **4a** from *M. hibiscifolia* (Benth.) Sch.-Bip.[10]

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[1] Work at The Florida State University was supported in part by a U.S. Public Health Service grant (CA-1312) through the National Cancer Institute.

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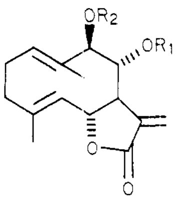
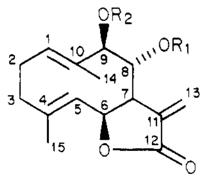


1a, R_1 = Epoxang; R_2 = Ac
b, R_1 = Ac; R_2 = Epoxang



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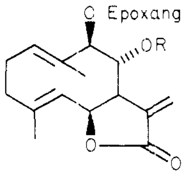
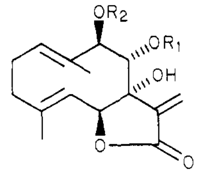
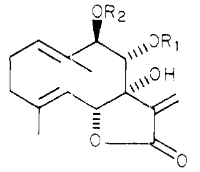


3a, R = H
b, R = Ac

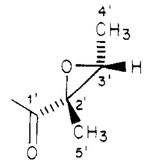


4a, R_1 = Epoxang; R_2 = Ac
b, R_1 = Ac; R_2 = Ac



5a, R_1 = Epoxang; R_2 = Ac
b, R_1 = Ac; R_2 = Epoxang

Epoxang =



The least polar lactone **2a**, $C_{22}H_{28}O_7$ (high-resolution mass spectrum), mp 193–194 °C, had IR bands at 1763 and 1655 cm^{-1} (α,β-unsaturated γ-lactone) and at 1725 and 1720 cm^{-1} (two ester carbonyls). The presence of acetate and epoxyangelate ester functions was revealed mass spectrometrically and by the ^1H and ^{13}C NMR spectra (Tables I and II); the similarity of ^1H NMR signals indicated that we were dealing with a lactone closely related to a noncrystalline substance from *M. pteropoda* previously assigned formula **1a** or **1b**.[3] A second somewhat more polar substance and the major lactone constituent, $C_{20}H_{26}O_6$ (**3a**), could not be obtained in crystalline form; the spectroscopic data showed the presence of a free secondary hydroxyl group and an epoxyangelate ester. Acetylation of **3a** furnished a noncrystalline acetate **3b** whose NMR spectrum was very similar to, though not identical with, the NMR spectrum of **2a**.

Spin decoupling of **2a** and **3a** in the usual way (Table I), with the H-13 signals as points of departure, permitted location of H-7 as a multiplet near 3 ppm and thence identification of H-6 and H-5 on the one hand and H-8 and H-9 on the other. H-8 of **3a** occurred at much higher field than H-8 of **2a** but moved downfield on acetylation to **3b**. Hence the lactone ring of **3a** was closed to C-6. In the case of **2a**, the direction of lactone ring closure was not as unambiguous but was inferred to be the same as that of **3a** and **3b** because of the similarity of chemical shifts and coupling constants. If that were so, nonidentity of **2a** and **3b** required the allocation of ester functions to C-8 and C-9 shown in formula **2a**.

Consideration of the small values of $J_{7,13}$ which require formulas based on a germacradienolide skeleton with a cis-lactone ring closed to C-6 or a heliangolide[11] and examination of Dreiding models showed that the magnitudes of $J_{5,6}$ and $J_{6,7}$ were in keeping with *trans,trans*-germacra-1(10),4-*cis*-6,12-olides rather than with heliangolides. Since $J_{7,8}$ and $J_{8,9}$ were large, the stereochemistry at C-8 and C-9 depicted in the formulas followed. Because **2a** is crystalline and **3b** is not, we assumed that **3b** was identical with the noncrystalline lactone previously[3] ascribed formula **1a** or **1b**.

The third and most polar lactone, $C_{22}H_{28}O_8$, mp 166–167 °C, also contained epoxyangelate and acetate ester functions but differed from **2a** in having an extra hydroxyl group (IR spectrum). The most noteworthy feature of the ^1H NMR spectrum was the absence of an H-7 proton, a feature indicated also by the appearance of the H-13 signals as singlets. In the ^{13}C NMR spectrum, the typical C-7 doublet in the range 45–50 ppm was replaced by a singlet near 83 ppm; consequently the hydroxyl group was attached to C-7. This substance was undoubtedly identical with one of the two isomers from *M. pteropoda* to which Bohlmann and LeVan[3] assigned structures **5a** and **5b**; by analogy with **2a** and **3a** (Tables I and II), we presumed that the actual structure was either **4a** or **4b** although the absence of $J_{7,13}$ couplings negated use of the arguments employed for deducing the structure of its congeners **2a** and **3a**. Partial hydrolysis to establish the distribution of the two ester functions over C-8 and C-9 was not successful.

In order to verify the formulations of **2a** and **3a** as cis lactones and to decide between the two possibilities, **4a** and **4b**, for the third lactone, X-ray analyses of **2a** and the third lactone were undertaken. The results showed that formulas **2a** and **4a** were correct.

Crystal data for **2a** and **4a** are given in Table III. Figure 1 contains two stereoscopic drawings of **4a** which probably represent the absolute configuration (vide infra). The first is a conventional drawing with the thermal ellipsoids; the second is another representation of the molecule in a different orientation which displays the chair–boat conformation adopted by the molecule in the solid state. The ring double bonds are trans, and the lactone ring is cis, is closed to C-6, and is a slightly distorted envelope with C-6 as the flap. The methyl groups are syn and below the plane of the ten-membered ring. The epoxyangelate is attached to C-8 and the acetate to C-9.

The structure of **2a** differs from that of **4a** only in the absence of the hydroxyl group from C-7 and is not reproduced in detail. Tables V–XII listing final atomic and final anisotropic thermal parameters, bond lengths, bond angles, and selected torsion angles of **2a** and **4a** are available as supplementary material. Comparison of the torsion angles shows that the conformations of **2a** and **4a** are quite similar. It is interesting that despite this similarity, crystals of **2a** are orthorhombic and those of **4a** monoclinic.

The following argument in favor of the absolute configuration as specified in Figure 1 can be given. In costunolide and other *trans,trans*-germacra-1(10),4-dien-*trans*-6,12-olides of established absolute configuration, i.e., with H-7 α, interaction between the double bonds in the ten-membered ring gives rise to a strongly *positive* Cotton effect below 215 nm.[13] If models representing these

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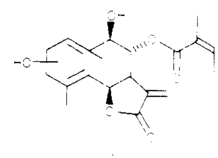
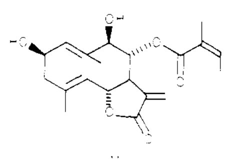
[10] On the basis of the published data, formula i for tomentosin seems as likely as that suggested by Geissman and Griffin[2] since several low-field NMR signals were apparently not resolved satisfactorily at 60 MHz. On the other hand, stereochemistry ii reported for montafrusin from *M. frutescens* (Mairet) Hemsl,[4] appears to be correct.



i



ii

[11] Lactone type A of ref 8b.

[12] That compounds **2a**, **3a**, and **4a** were not heliangolides would theoretically have followed also from the absence of an NOE involving H-5 and H-15. In practice, the absence of this NOE could not be established unambiguously due to the closeness of the H-5, H-6, and H-9 signals.

Table I. ^{1}H NMR Spectra of *M. hibiscifolia* Constituents[a]

	2a	2a[b]	3a	3b	4a
H-1	5.48 br t (8)	5.07 tq (8, 1)	5.38 br t (7.5)	5.48 br t (8)	5.37 m
H-2	2–2.4 m	2–2.4 m	2–2.4 m	2.1–2.4 m	2.1–2.4 m
H-3	2–2.4 m	2–2.4 m	2–2.4 m	2.1–2.4 m	2.1–2.4 m
H-5	5.12[c]	4.84 br d (11)	4.96 br d (11)	5.12[c]	4.97 br d (10.5)
H-6		4.53 dd (6, 11)	5.16 dd (11, 6)		4.91 d (10.5)
H-7	3.24 m	2.65 br dd (6, 8.5)	3.16 m	3.22 m	
H-8	5.38 dd (8.5, 9.5)	5.46 dd (8.5, 9.5)	4.10 t (8)	5.30 dd (8, 9)	5.36[c]
H-9	4.96 d (9.5)	4.95 d (9.5)	4.83 d (8)	5.11 d (9)	
H-13a	6.38 d	6.31 br	6.34 br	6.35 d (1)	6.43
H-13b	5.72 d (1)	5.29 br	5.77 br	5.67 br	5.99
H-14	1.67 d (1)	1.11 d (1)	1.65 br	1.66 br	1.77 br
H-15	1.71 br	1.19 br	1.77 br	1.72 br	1.72 d (1)
H-3′	2.98 q (5.5)	2.54 q (5.5)	3.06 q (5.5)	3.01 q (5.5)	2.98 q (5.5)
H-4′	1.29 d (5.5)	1.23 d (5.5)	1.34 d (5.5)	1.27 d (5.5)	1.29 d (5.5)
H-5′	1.46	1.31	1.58	1.51	1.46
Ac	1.99	1.67		1.93	1.98

[a] Run at 270 MHz in $CDCl_3$ with Me_4Si as internal standard. Chemical shifts are in parts per million; figures in parentheses are coupling constants in hertz. [b] In C_6D_6. [c] Center of AB system.

Table II. ^{13}C NMR Spectra of *M. hibiscifolia* Constituents[a]

	2a	3a	4a
C-1	131.28 d[b]	130.25 d	131.92 d
C-2	25.06 t	25.11 t	24.92 t
C-3	38.71 t	38.74 t	38.96 t
C-4	135.21	135.55	135.54
C-5	122.89 d[b]	123.43 d	122.21 d[b]
C-6	70.25 d[b]	68.36 d	83.37 d[b]
C-7	46.60 d	47.83 d	82.77
C-8	78.66[c]	82.75[c]	77.08[c]
C-9	74.99[c]	76.10[c]	75.01 d[c]
C-10	138.53	138.12	140.77[d]
C-11	133.90	134.69	140.24[d]
C-12	169.52	170.52	169.93
C-13	126.69 t	126.68 t	127.70 t
C-14	19.18 q	19.19 q	17.99 q
C-15	16.95 q	16.96 q	16.86 q
C-1′	168.84[d]	169.06	168.28[e]
C-2′	59.65	60.08	59.62
C-3′	59.76 d[b]	60.25 d	60.12 d
C-4′	14.06 q[b]	13.86 q	13.90 q
C-5′	19.18 q[b]	19.19 q	19.06 q
C-1″ (Ac)	168.18[d]		167.86[e]
C-2″ (Ac)	21.03 q		21.32 q

[a] Run at 67.09 MHz in $CDCl_3$ with Me_4Si as internal standard. Values are in parts per million. Unmarked signals are singlets. [b] Assignments verified by single-frequency off-resonance spin decoupling. [c,d,e] Assignments may be interchanged.

Table III. Crystal Data for 2a and 4a

	2a	4a
formula	$C_{22}H_{28}O_7$	$C_{22}H_{28}O_8$
fw	404.46	420.46
space group	$P2_12_12_1$	$P2_1$
a, Å	9.904 (2)	10.155 (2)
b, Å	10.329 (3)	18.010 (3)
c, Å	21.238 (4)	5.978 (2)
β, deg		91.52 (2)
Z	4	2
d_{calcd}, g cm^{-3}	1.236	1.277
μ(Cu Kα), cm^{-1}	7.7	8.2

Table IV. Lactone Ring Torsion Angles (deg)

		2a	4a
C(6)-O(1)-C(12)-C(11)	ω_1	9.8	6.6
C(13)-C(11)-C(12)-O(2)	ω_2	15.0	17.2
C(11)-C(7)-C(6)-O(1)	ω_3	29.5	26.5
C(5)-C(6)-C(7)-C(8)	ω_4	28.7	27.9

molecules are viewed from the front and through the C-4, C-5 bond, the angle which the plane of the C-4, C-5 double bond makes with the plane of the C-1, C-10 double bond in the rear is negative. Contrariwise, compounds **2a**–**4a** exhibit strongly *negative* Cotton effects below 215 nm. Inspection of Figure 1 shows that the angle which the plane of the C-4, C-5 double bond in front makes with the plane of the C-1, C-10 double bond in the rear is positive and opposite in sign to that found in costunolide as required by the CD curve. Hence Figure 1 is likely to depict the absolute configuration of **4a** and its congeners.

Compounds **2a**–**4a** also display positive Cotton effects near 250 nm associated with the n,π^* transition of the α,β-unsaturated lactone. On the assumption that Figure 1 actually represents the absolute configuration of **2a**–**4a**, the generalization[14] that chirality of the –C=C—C=O chromophore (ω_2) determines the sign of the lactone n,π^* Cotton effect appears to hold in this series, as indicated by the lactone ring torsion angles given in Table IV.[15]

While our study was nearing completion, there appeared a communication on several lactones from *Ursinia anthemoides* (L.) Poiret[16] which showed that these substances were also *trans,trans*-germacra-1(10),4-dien-*cis*-6,12-olides.[17] Similar arguments were used to deduce the absolute configuration.

Experimental Section

Isolation of 2a, 3a, and 4a. Above-ground parts of *Montanoa hibiscifolia* (Benth.) Sch.-Bip. (12 kg), collected by Mr. G Cruz near Tegucigalpa, Honduras, in the fall of 1975 (voucher on deposit in herbarium of UNAH, accession no. P.R.-80865 of Medicinal Plant Resources Laboratory, USDA), were extracted with $CHCl_3$ and worked up as usual.[18] The crude gum (76 g) was preadsorbed on 160 g of silicic acid (Mallinckrodt, 100 mesh) and loaded onto 750 g of silicic acid packed in the solvent system toluene–$CHCl_3$ (3:1). The column was eluted with 1-L fractions as follows: fractions 1–6 (toluene–$CHCl_3$, 3:1), 7–16 ($CHCl_3$), 17–25 ($CHCl_3$–MeOH, 97:3). Fraction 9 on trituration with benzene deposited solid material (**2a**, 0.8 g) which was recrystallized from $CHCl_3$–benzene: mp 193–194 °C; $[\alpha]_D$ –200° (*c* 0.0558, $CHCl_3$);

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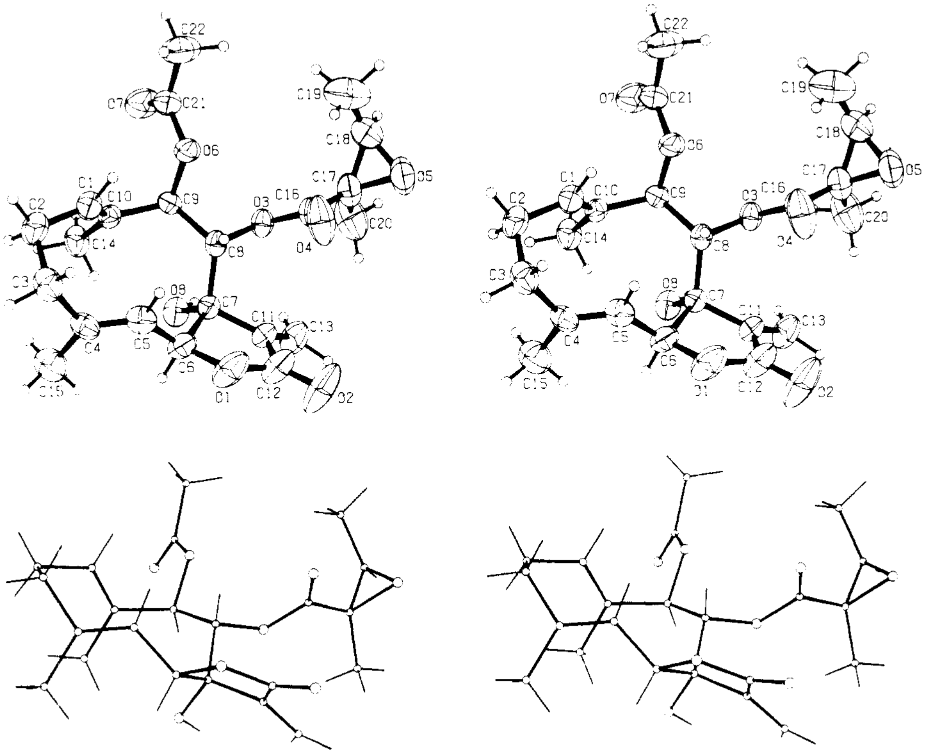

Figure 1. Stereoscopic view of **4a**.

UV (MeOH) λ_{max} 210 nm (ϵ 15000); IR (KBr) 3075 (olefinic CH), 1763 (γ-lactone), 1725 and 1720 (ester carbonyls), 1655 cm^{-1} (double bonds); CD (MeOH) $[\Theta]_{254}^{max}$ +5360, $[\Theta]_{216}$ −70200 (last reading). The molecular ion was very weak; other significant peaks in the high-resolution mass spectrum appeared at *m/e* (composition, %) 246 ($C_{15}H_{18}O_3$, 48.1), 228 ($C_{15}H_{16}O_2$, 72.2), 116 ($C_5H_8O_3$, 52.5), and 105 (C_8H_9, 100).

Anal. Calcd for $C_{22}H_{28}O_7$: mol wt 404.1835. Found: mol wt (mass spectrum) 404.1862.

Fractions 11–16 which showed only one major spot on TLC were combined. The gummy lactonic constituent **3a** (12.5 g) was isolated by preparative TLC (silica gel GF254, $CHCl_3$–MeOH, 47:3). The material obtained in this fashion was not completely pure as indicated by additional weak signals in the ^1H and ^{13}C NMR spectrum which could not be removed by further chromatography. Substance **3a** had the following: IR 3470 (OH), 1760 (γ-lactone), 1740 (ester), 1660 cm^{-1} (double bonds); UV (MeOH) λ_{max} 211 nm (ϵ 13000); CD $[\Theta]_{250}^{max}$ +2900, $[\Theta]_{218}$ −48500 (last reading). The molecular ion was quite weak; other significant peaks in the high-resolution mass spectrum were at *m/e* (composition, %) 246 ($C_{15}H_{18}O_3$, 29.8), 228 ($C_{15}H_{16}O_2$, 53.6), 213 ($C_{14}H_{13}O_2$, 39.2), 121 (C_9H_{13}, 100), and 116 ($C_5H_8O_3$, 63.3).

Anal. Calcd for $C_{20}H_{26}O_6$: mol wt 362.1728. Found: mol wt (mass spectrum) 362.1734.

Acetylation of 0.1 g of **3a** in 0.5 mL of pyridine with 0.2 mL of acetic anhydride and workup after 24 h gave **3b** which remained noncrystalline after preparative TLC (MeOH–$CHCl_3$, 1:19), yield 0.85 g, and which exhibited the ^1H NMR spectrum reported in Table II.

Fractions 18 and 19 (4 g) showed one major spot on TLC. Preparative TLC of the combined fractions ($CHCl_3$–MeOH, 43:3) gave 1.5 g of **4a** which was recrystallized from EtOAc and melted at 166–167 °C (lit[3] mp 162 °C); $[\alpha]_D$ −216.5° (*c* 0.041, $CHCl_3$); UV (MeOH) λ_{max} 211 nm (ϵ 14800); IR 3420 (OH), 1770 (γ-lactone), 1730 (two esters), 1660 cm^{-1} (double bonds); CD (MeOH) $[\Theta]_{260}$ +730, $[\Theta]_{252}^{infl}$ +850, $[\Theta]_{242}^{max}$ +1050, $[\Theta]_{224}$ −22000 (last reading). The molecular ion was very weak; other significant peaks in the high-resolution mass spectrum appeared at *m/e* (composition, %) 262 ($C_{15}H_{18}O_4$, 21.2), 244 ($C_{15}H_{16}O_3$, 50.8), and 226 ($C_{15}H_{14}O_2$, 24.8).

Anal. Calcd for $C_{22}H_{28}O_8$: mol wt 420.1784. Found: mol wt (mass spectrum) 420.1743.

X-ray Analyses. Signal crystals of **2a** were prepared by slow crystallization from $CHCl_3$–benzene. The intensity data were measured on a Hilger-Watts diffractometer (Ni filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). A crystal measuring approximately 0.25 × 0.4 × 0.6 mm was used for data collection; the data were not corrected for absorption. A total of 1706 reflections were measured for $\theta \leq 57°$ of which 1626 were considered to be observed [$I > 2.5(\sigma I)$]. The structure was solved by a multiple-solution procedure[19] and was refined by full-matrix least-squares methods. In the final refinement, anisotropic thermal parameters were used for the heavier atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were used in the structure factor calculations, but their parameters were not refined. The final discrepancy indices were $R = 0.032$ and $R_w = 0.041$ for the 1626 observed reflections. The final difference map had no peaks greater than ±0.1 Å^{-3}.

Single crystals of **4a** were prepared by slow crystallization from EtOAc. The procedure used was the same as in the preceding paragraph with a crystal of approximately 0.4 × 0.6 × 0.8 mm, no absorption correction, and 1530 reflections of which 1493 were considered to be observed. The final discrepancy indices were $R = 0.042$ and $R_w = 0.053$ for the 1493 observed reflections. The final difference map had no peaks greater than ±0.2 Å^{-3}.

Registry No. 2a, 72690-77-8; **3a**, 72638-72-3; **3b**, 72638-73-4; **4a**, 72690-78-9.

Supplementary Material Available: Tables V and VI listing final atomic and anisotropic thermal parameters, respectively, for **2a**, Tables VII and VIII listing final atomic and anistropic thermal parameters, respectively, for **4a**, and Tables IX, X, and XI listing bond lengths, bond angles, and selected torsion angles, respectively, for **2a** and **4a** (9 pages). Ordering information is given on any current masthead page.

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(19) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368.