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MOLECULAR REARRANGEMENTS IN THE LONGIPINENE SERIES

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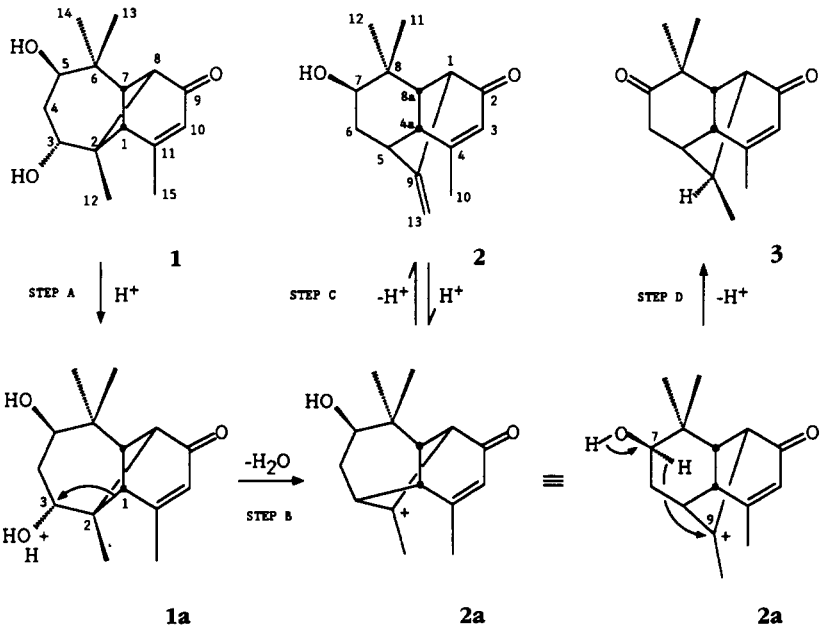
ABSTRACT.—The longipinene derivative **1** affords the moreliane derivatives **2** and **3** in acid, the former by Wagner-Meerwein rearrangement and the latter by subsequent transannular hydride migration. Compound **2** can be prepared selectively by rearrangement of monoester **9** followed by hydrolysis. The kinetics of **10**, **20**, and **27** to afford **13**, **23**, and **30**, respectively, reveal that the dihydroderivatives **20** and **27** rearrange faster than the unsaturated compound **10**; this is attributed to steric interaction between several atoms of the six- and four-membered rings in the dihydroderivatives. Kinetics of the hydride migration from **2**, **21**, and **29** to afford **3**, **24**, and **31**, respectively, show that rearrangement of unsaturated compound **2** is slower than for the dihydroderivatives. This can be explained by a stabilizing electronic interaction between the 3,4 double bond and the carbonium ion at C-9 in **2a**. Structures of the rearranged substances were determined by chemical correlation and by single crystal X-ray diffraction of **2**.

Minor structural modifications on chemical pathways of molecular rearrangements have been highlighted recently, in particular for bicyclic structures (1–5). We recently explored the Wagner-Meerwein rearrangement of the sesquiterpenoid rastevione [**4**] into moreli-9-ene-6α,7β-diol-2-one [**8**] (6). We now report acid-catalyzed rearrangements of the longipinene derivatives **1**, **9**, **10**, **16**, **18**, **19**, **20**, **26**, and **27**. Although closely related, these compounds show significant differences in reactivity during rearrangement. It should also be noted that the structural drawings and numbering used herein are different from those used in earlier papers (7–9), but they are in agreement (6) with *Chemical Abstracts* usage.

RESULTS AND DISCUSSION

p-Toluenesulfonic acid catalyzed rearrangement of diol **1** (7) gave a mixture of dienolone **2** and endione **3**. Compound **2** is formed (Scheme 1) when the protonated hydroxyl group at C-3 in **1a** is displaced by the antiperiplanar C-1,C-2 bond (step B) followed by deprotonation of carbonium ion **2a** (step C). Endione **3** is also formed from carbonium ion **2a** but by a transannular hydride migration (10) from C-7 to C-9 (step D). The reversibility of step C became evident when the reaction time was increased from 2 to 6 h, because the only product was **3**. Pure **2** was completely transformed into **3** under the same reaction conditions. Because an ester group at C-5 precludes hydride migration, the *p*-nitrobenzoate **9** was allowed to react under the rearrangement conditions to afford **12**, which was then treated with KOH in MeOH to give **2**. Hydride migration was confirmed by isotopic labeling. Deuterodiol **16** was prepared by oxidation of 3-monoacetate **11** (8) with CrO_3 in HOAc to afford diketone **15**, which was then treated with $LiAlD_4$ and hydrolyzed. *p*-Toluenesulfonic acid treatment of **16** in C_6H_6 for 9 h afforded deuteroendione **17** as the only product.

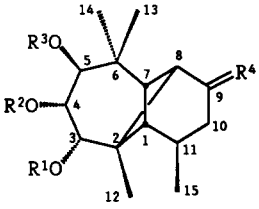
Treatment of dihydroderivative **18** under the rearrangement conditions gave only diketone **24**, but when the reaction time was decreased from 2 to 0.5 h, a mixture of **21** and **24** was obtained. Using analogous procedures pure **21** was transformed into **24**, and selective preparation of **21** was carried out from **19** to afford **22**, which was then



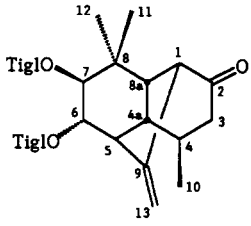
SCHEME 1. Transformation of longipinene derivative **1** to moreliene derivatives **2** and **3**.

hydrolyzed. These results reveal that dihydroderivative **18** rearranges similarly to diol **1**, but one or more of the reaction steps is faster.

At this point the dihydroderivative **26**, which is epimeric at C-11 of **18**, was prepared for the purpose of conducting comparative kinetic measurements that allowed evaluation of reaction rate differences caused either by changes in the stereochemistry at C-11 or by the electron density at the 10,11 bond in the longipinene skeleton. Com-



4 R^1=H, R^2=R^3=Ang, R^4=O
5 R^1=R^3=H, R^2=Ts, R^4=O
6 R^1=R^3=Ac, R^2=Ts, R^4=O
7 R^1=R^3=Ac, R^2=Ts, R^4=OCH_2CH_2O



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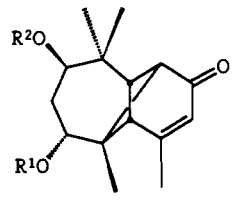
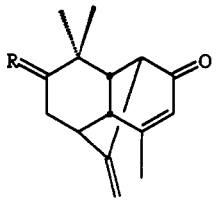
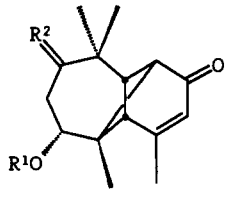


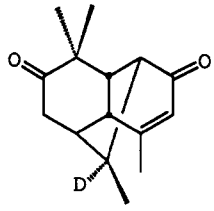
9 R^1=H, R^2=*p*-NO_2Bz
10 R^1=H, R^2=Ac
11 R^1=Ac, R^2=H



12 R=(—O*p*-NO_2Bz, —H)
13 R=(—OAc, H)
14 R=O



15 R^1=Ac, R^2=O
16 R^1=H, R^2=(—OH, —D)



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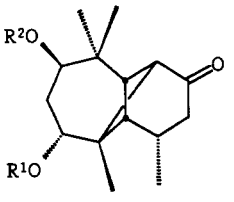
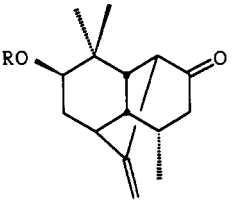
pound **26** was prepared by acetylation of **5** (7) to yield the diacetate tosylate **6** which was treated with ethylene glycol and *p*-toluenesulfonic acid to give the ethyleneketal **7**. Reduction of **7** with $LiAlH_4$ followed by removal of the ethyleneketal group with HCl in Me_2CO afforded diol **26**. When **26** was treated under the rearrangement conditions, it reacted faster than the unsaturated compound **1**, and produced **29** and **31**.

For kinetic studies, separate measurements for the Wagner-Meerwein rearrangement steps (A, B, and C) and for the hydride migration (steps C and D) were done. This was achieved using the C-5 monoacetates **10** (8), **20**, and **27**. Compound **20** was obtained by catalytic hydrogenation of **10**, while **27** was obtained by treatment of diol **26** with 1.2 equiv of acetyl chloride. The monoacetates **10**, **20**, and **27**, when treated under the same reaction conditions, afforded compounds **13**, **23**, and **30**, respectively, as sole products, allowing kinetic measurement of the first part of the transformation. On the other hand, hydrolysis of **13**, **23**, and **30** gave **2**, **21**, and **29**, respectively, allowing kinetic measurement of the hydride migration. The kinetics were followed by ^{1}H-nmr measurements and allowed estimation of the relative rates for the rearrangements of **10**, **20**, and **27** which are 1.0, 5.9, and 4.6, respectively. The marked differences between the unsaturated (1.0) and the saturated (5.9 and 4.6) compounds may be explained by inspection of molecular models. The saturated compound **20** has large steric hindrances between methyl groups at C-2 and C-11, and between the methyl group at C-2 and the alpha hydrogen atom at C-10, which are released when rearrangement occurs. This effect is also observed in dihydroderivative **27** (4.6), where steric hindrance exists between H-11 and the methyl group at C-2 and between H-10β and H-7.

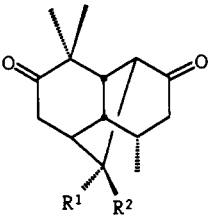
Relative rates of hydride migration from **2**, **21**, and **29** are 1.0, 6.4, and 7.8, respectively. The noticeable differences between the unsaturated and the saturated com-



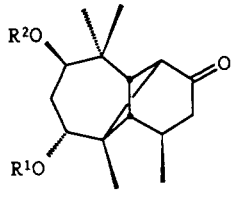
18 $R^1=R^2=H$
19 $R^1=H$, $R^2=p$-NO_2Bz
20 $R^1=H$, $R^2=Ac$



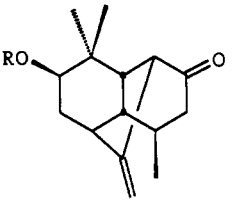
21 R=H
22 R=*p*-NO_2Bz
23 R=Ac



24 $R^1=H$, $R^2=Me$
25 $R^1=Me$, $R^2=H$



26 $R^1=R^2=H$
27 $R^1=H$, $R^2=Ac$
28 $R^1=R^2=Ac$



29 R=H
30 R=Ac

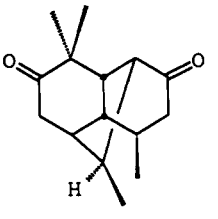


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TABLE 1. ^{1}H-nmr Chemical Shifts,[a] Multiplicities,[b] and Coupling Constants[b] for Longipinene Derivatives.

Proton	Compound								
	6[c]	**7**[d]	**15**[e]	**16**[f]	**19**[h]	**20**[i]	**26**[j]	**27**[k]	**28**[l]
H-1	2.19	1.86	2.94	2.68	2.32	2.22	2.04	2.06	2.14
H-3	5.27	5.17	5.13	3.78	3.90	3.78	3.74	3.75	4.85
H-4α	5.02	4.95	2.70	1.85	2.02	1.85	1.85	1.85	1.98
H-4β			3.27	2.25	2.46	2.28	2.26	2.26	2.15
H-5	5.32	5.29	—	—	5.35	5.00	3.90	5.02	4.95
H-7	1.85	1.66	2.41	2.19	1.70	1.58	1.74	1.75	1.79
H-8	2.96	2.33	2.97	2.94	3.10	2.99	2.90	2.98	3.03
H-10α	2.14	1.69	5.87	5.66	2.25	2.22	2.13	2.13	2.15
H-10β	2.56	2.18			2.95	2.90	2.53	2.55	2.57
H-11	2.35	2.20	—	—	2.34	2.34	2.29	2.31	2.34
H-12	0.85	0.95	1.05	1.05	1.20	1.14	0.98	1.00	0.89
H-13	1.06	1.00	1.05	0.95[g]	1.20[g]	1.00	1.01	0.99	1.00
H-14	0.93	0.94	1.22	0.93[g]	0.96[g]	0.88	0.92	0.92	0.93
H-15	1.11	0.98	2.13	2.03	1.24	1.20	1.08	1.09	1.11

[a]In ppm at 300 MHz from $CDCl_3$ solutions with the exception of **16**, which was measured from $(CD_3)_2CO$ solution.

[b]Couplings are in Hz: H-1 for **6**, **7**, and **26–28** (br d, $J = 6$), for **15** and **16** (dd, $J = 1, 7$), for **19** and **20** (ddd, $J = 1, 3, 6$). H-3 for **6** and **7** (d, $J = 3$), for **15** (dd, $J = 4, 5$), for **16**, **19**, **20**, and **26–28** (t, $J = 4$). H-4 for **6** and **7** (dd, $J = 3, 11$). H-4α for **15** (dd, $J = 5, 13$), for **16** (dd, $J = 4, 14$) for **19**, **20**, and **26–28** (ddd, $J = 2, 4, 15$). H-4β for **14** (dd, $J = 4, 13$), for **16** (br d, $J = 14$) for **19**, **20**, **26–28** (ddd, $J = 3, 12, 15$). H-5 for **6** and **7** (d, $J = 11$), for **19**, **20**, and **26–28** (dd, $J = 2, 12$). H-7 (br s). H-8 for **6**, **7**, **17**, and **26–28** (d, $J = 6$), for **15** and **16** (dd, $J = 1, 7$). H-10 for **15** and **16** (sextet, $J = 1$). H-10α for **6** and **26–28** (dd, $J = 6, 19$), for **7** (m overlapped by H-11), for **19** and **20** (dd, $J = 5, 20$). H-10β for **6** and **26–28** (dd, $J = 10, 19$), for **7** (m overlapped by H-7), for **19** and **20** (dd, $J = 10, 20$), H-11 (m). H-12 (s, 3H). H-13 (s, 3H). H-14 (s, 3H). H-15 for **6**, **7**, **19**, **20**, and **26–28** (d, 3H, $J = 7$), for **15** and **16** (d, 3H, $J = 1$).

[c]Tosylate: 7.75 (d, $J = 8$), 7.35 (d, $J = 8$), and 2.44 (s). Acetates: 2.04 (s) and 2.00 (s).

[d]Tosylate: 7.75 (d, $J = 8$), 7.33 (d, $J = 8$), and 2.44 (s). Ethylene ketal: 3.97–3.73 (complex m). Acetates: 2.04 (2s).

[e]Acetate: 2.07 (s).

[f]3-OH: 4.03 (d, $J = 5$). 5-OH: 3.51 (br s).

[g]May be interchanged.

[h]*p*-NO_2-benzoate: 8.37 (d, $J = 9$) and 8.25 (d, $J = 9$). OH: 2.30 (br s).

[i]Acetate: 2.06 (s). OH: 2.40 (br s).

[j]3-OH and 5-OH: 2.30 (br s).

[k]Acetate: 2.07 (s). OH: 1.60 (br s).

[l]Acetates: 2.14 (s) and 2.04 (s).

pounds may be explained in terms of electronic stabilizing interactions between the double bond at C-3,C-4 and the carbonium ion at C-9 in structure **2a**.

Structures were deduced from ^{1}H- and ^{13}C-nmr spectra; assignments were made with the aid of COSY for **3**, **21**, **24**, and **25**, ^{13}C-^{1}H heteronuclear chemical shift correlation diagrams for **3**, **6**, **7**, **12**, **20**, **21**, **24**, and **31**, and coupled ^{13}C-nmr spectra for **13**, **15**, **19**, and **22**. The ^{1}H-nmr data are summarized in Tables 1 and 2 and the ^{13}C-nmr data in Tables 3 and 4. Regarding the ^{13}C-nmr assignments in Table 4, it has to be noted that the assignments for C-4a and C-8a have been reversed from our previous assignments (6) in light of an analysis of substituent effects.

By examining the ^{1}H-nmr spectra of diketones **3**, **24**, and **31**, it was found that H-6β has a long range coupling of 1 Hz with H-9 even though these two protons are not in a W-type arrangement. This could be considered in disagreement with the

TABLE 2. ^{1}H-nmr Chemical Shifts,[a] Multiplicity,[b] and Coupling Constants[b] for Moreliene Derivatives.

Proton	Compound														
	2[c,d]	**3**[c]	**3**[e]	**12**[c,f]	**13**[c,g]	**14**[c]	**17**[c]	**21**[c,h]	**22**[c,j]	**23**[c,k]	**24**[c]	**25**[e]	**29**[c,l]	**30**[c,m]	**31**[c]
H-1	3.40	3.06	3.02	3.53	3.46	3.50	3.04	3.29	3.45	3.37	2.86	2.51	3.29	3.35	2.86
H-3α	5.62	5.81	5.71	5.67	5.63	5.71	5.81	2.25	2.30	2.28	1.90	1.76	2.68	2.70	2.41
H-3β								2.07	2.22	2.09	2.49	2.12	1.81	1.81	1.98
H-4	—	—	—	—	—	—	—	1.99	2.07	1.98	2.13	1.55	2.00	2.02	2.04
H-4a	2.64	2.84	2.12	2.76	2.67	3.02	2.82	2.15	2.30	2.18	2.31	1.88	2.07	2.11	2.26
H-5	2.66	2.03	1.33	2.77	2.68	2.88	2.01	2.88	3.01	2.91	2.11	1.84	2.64	2.66	1.94
H-6α	2.06	2.57	2.19	2.32	2.14	2.52	2.57	1.93	2.16	2.03	2.59	1.90	1.92	1.99	2.45
H-6β	1.70	2.68	2.01	1.87	1.69	2.82	2.67	1.60	1.80	1.60	2.52	2.27	1.66	1.66	2.66
H-7	3.64	—	—	5.12	4.82	—	—	3.55	5.11	4.79	—	—	3.54	4.76	—
H-8a	2.08	2.28	1.82	2.17	2.08	2.31	2.27	1.71	1.84	1.74	1.91	1.32	1.81	1.92	2.11
H-9	—	2.02	1.63	—	—	—	—	—	—	—	1.83	1.66	—	—	1.90
H-10	1.99	2.11	1.42	2.04	2.00	2.10	2.11	1.03	1.10	1.04	1.12	0.64	1.02	1.02	1.14
H-11	0.98	1.17	0.91	1.02	0.93	1.21	1.17	0.99[i]	1.04	0.93	1.19	1.03	0.98	0.94	1.19
H-12	1.02	1.08	0.76	1.23	1.04	1.07	1.08	1.00[i]	1.27	1.05	1.06	0.83	1.04	1.03	1.08
H-13	5.16	0.92	0.76	5.31	5.24	5.32	0.93	4.98	5.15	5.07	1.04	0.69	5.35	5.11	0.97
H-13′	5.02	—	—	5.17	5.10	5.13	—	4.93	5.11	5.04	—	—	5.22	5.11	—

[a]In ppm at 300 MHz.

[b]Couplings are in Hz: H-1 for **2**, **12–14**, **17**, **21–23**, **25**, **29**, and **30** (br s), for **3**, **24**, and **31**, (br d, $J = 8$ Hz). H-3 for **2**, **3**, **12–14**, and **17** (quintet, $J = 1$ Hz). H-3α for **21–23** (dd, $J = 12$, 16), for **24** and **25** (dd, $J = 11$, 17), for **29** and **30** (dd, $J = 9$, 17), for **31** (complex m). H-3β for **21–23** (dd, $J = 7$, 16), for **24** and **25** (dd, $J = 8$, 17), for **29** and **30** (dd, $J = 4$, 17), for **31** (complex m). H-4 (m). H-4a (br m). H-5 (br m). H-6α for **2**, **12**, **13**, **21–23**, **29**, and **30** (ddd, $J = 6$, 6, 12), for **3**, **24**, and **31** (dd, $J = 4$, 17), for **14** (dd, $J = 4$, 16), for **17** (dd, $J = 4$, 17), for **25** (ddd, $J = 1$, 4, 17). H-6β for **2**, **12**, **13**, **21–23**, **29**, and **30** (ddd, $J = 2$, 12, 12), for **3**, **24**, and **31** (ddd, $J = 1$, 3, 17), for **14** (dd, $J = 3$, 16), for **17** (dd, $J = 3$, 17), for **25** (br dd, $J = 3$, 17). H-7 (dd, $J = 6$, 11). H-8a (br s). H-9 (br quintet, $J = 7$). H-10 for **2**, **3**, **12–14**, and **17** (d, $J = 1$), for **21–25**, and **29–31** (d, $J = 7$). H-11 (s). H-12 (s). H-13 for **2**, **12–14**, **17**, **21–23**, **29**, and **30** (br s), for **3**, **24**, **25**, and **31** (br d, $J = 7$). H-13′ (br s).

[c]From $CDCl_3$ solutions.

[d]OH: 1.34 (br s).

[e]From C_6D_6 solutions.

[f]*p*-NO_2-benzoate: 8.30 (d, $J = 9$) and 8.17 (d, $J = 9$).

[g]Acetate: 2.03 (s).

[h]OH: 2.46 (br s).

[i]May be interchanged.

[j]*p*-NO_2-benzoate: 8.30 (d, $J = 9$) and 8.18 (d, $J = 9$).

[k]Acetate: 2.02 (s).

[l]OH: 1.30 (br s).

[m]Acetate: 2.02 (s).

TABLE 3. ^{13}C-nmr Chemical Shifts[a] for Longipinene Derivatives.

Carbon	Compound								
	6[b]	**7**[c]	**15**[d]	**16**	**19**[f]	**20**[g]	**26**	**27**[h]	**28**[i]
C-1	44.5	44.3	48.9	49.5	45.4	45.3	44.8	44.9	44.6
C-2	45.4	43.8	56.0	57.7	46.0	45.8	47.3	47.2	45.9
C-3	75.1	76.6	74.5	73.7	73.7	73.7	74.0	73.7	75.5
C-4	76.6	77.3	41.5	40.0	35.8	35.8	39.0	35.8	32.0
C-5	70.3	71.0	209.0	68.8[e]	75.1	73.0	69.8	73.1	73.1
C-6	34.9	34.5	47.8	38.9	36.8	36.3	36.8	35.9	35.8
C-7	46.0	47.7	63.3	67.4	53.2	53.1	46.5	46.5	46.3
C-8	52.3	42.8	54.8	53.6	51.9	51.9	52.0	52.1	52.9
C-9	210.6	113.5	202.1	203.6	211.8	212.0	214.0	212.2	211.9
C-10	41.7	39.6	123.0	122.9	41.7	41.7	42.2	42.1	41.9
C-11	26.7	28.3	169.6	172.0	33.1	33.0	27.1	26.8	26.8
C-12	19.7	20.7	21.3	22.2	22.7	22.7	20.5	20.4	20.1
C-13	19.5	19.6	22.1	18.2	18.9	18.6	17.7	18.8	18.7
C-14	26.9	26.6	24.5	26.9	26.7	26.6	27.2	26.9	26.7
C-15	19.6	20.7	23.5	23.2	21.0	20.9	19.7	19.8	19.7

[a]In ppm at 75.4 MHz from $CDCl_3$ solutions with the exception of **13** measured from $(CD_3)_2CO$ solution.

[b]Tosylate: 144.9, 133.8, 129.7, 127.8, and 21.6. Acetates: 170.0, 169.9, 20.7, and 20.6.

[c]Tosylate: 144.7, 134.1, 129.6, 127.9, and 21.7. Acetates: 170.5, 170.1, 20.9, and 20.8. Ethylene ketal: 64.7 and 62.9.

[d]Acetate: 170.3 and 21.0.

[e]Small 1:1:1 triplet due to C(5)-D coupling.

[f]*p*-NO_2-benzoate: 164.2, 150.6, 136.0, 130.6, and 123.6.

[g]Acetate: 170.9 and 21.3.

[h]Acetate: 170.7 and 21.3.

[i]Acetates: 171.0, 170.3, 21.2, and 21.1.

stereochemistry of **3**, **24**, and **31** at C-9, but it is known that W arrangement of atoms is not a strict condition for long-range coupling in carbocyclic structures (11,12). In order to obtain further stereochemical support, alcohol **2** was oxidized with CrO_3 in HOAc at room temperature to afford diketone **14**. With the exception of the signals due to C-9 and C-13 (Table 4), the ^{13}C-nmr spectra of **14** and **3** are very similar; therefore, **2** and **3** possess the same carbon skeleton. In addition, an nOe experiment using diketone **3** in C_6D_6 showed that when H-9 is irradiated, the signal for H-6α is increased by 16% and the signal for H-1 is increased by 7%. This supports the stereochemistry in which H-9 is cis to H-1 and close to H-6α.

Further structural evidence of the rearranged substances was obtained by X-ray diffraction analysis of **2** and its chemical correlation with other rearranged substances (**3**, **21**, **24**, and **29**).

A perspective view of the molecular structure of **2** is depicted in Figure 1, and the experimentally refined final fractional atomic coordinates are listed in Table 5. Crystal data and collection and refinement parameters are in the Experimental section.

Finally, catalytic hydrogenation of **2** (5% Pd/C in MeOH) gave **21** and **29**, which were separated by chromatography and directly compared with the samples obtained from the rearrangement reactions. Similarly, catalytic hydrogenation of **21** with PtO_2 followed by oxidation with CrO_3 gave **24** and its C-9 epimer **25**. Diketone **24** was identical to the sample obtained by hydride migration of **21**. Catalytic hydrogenation of diketone **3** with 5% palladium over charcoal yielded **24** as the only product.

TABLE 4. ^{13}C-nmr Chemical Shifts[a] for Moreliene Derivatives.

Carbon	Compound													
	2	**3**	**12**[b]	**13**[c]	**14**	**17**	**21**	**22**[e]	**23**[f]	**24**	**25**	**29**	**30**[h]	**31**
C-1 . .	57.5	56.6	57.4	57.4	58.9	56.5	58.5	58.5	58.5[g]	58.1	58.9	58.7	58.6	56.7
C-2 . .	198.5	201.7	197.8	198.1	197.2	201.7	209.9	208.7	209.3	211.3	212.0	209.7	209.2	212.7
C-3 . .	123.9	125.9	124.2	124.1	124.3	125.9	42.3	42.3	42.3	44.7	42.7	41.9	41.8	43.4
C-4 . .	165.8	166.1	165.1	165.3	165.0	166.1	34.4	34.4	34.4	33.2	33.6	31.9	31.9	30.8
C-4a . .	48.9	50.6	48.8	48.8	49.1	50.6	46.6	46.7	46.6	49.4	49.1	46.8	46.8	48.7
C-5 . .	44.1	43.8	43.7	43.8	43.9	43.7	41.1	40.8	40.8	39.0	36.9	47.7	47.3	48.0
C-6 . .	39.0	47.6	35.4	35.4	47.4	47.6	40.2	36.6	36.6	50.5	43.8	40.1	36.4	49.2
C-7 . .	71.8	214.2	76.2	74.0	212.3	214.6	72.3	77.1	74.8	215.9	216.0	72.5	74.7	215.2
C-8 . .	38.6	47.9	38.1	37.7	48.2	47.6	38.8	38.4	38.0	48.3	48.4	38.3	37.4	47.4
C-8a . .	59.3	59.5	59.4	59.4	58.2	59.6	58.2	58.5	58.4[g]	56.8	57.1	52.1	52.5	51.2
C-9 . .	149.3	38.2	147.8	148.1	147.0	—[d]	152.3	150.9	151.0	38.7	38.2	150.5	149.4	38.2
C-10 . .	23.2	23.4	23.2	23.1	23.2	23.4	19.3	19.4	19.6	19.9	19.7	22.3	22.2	23.6
C-11 . .	25.3	27.0	25.5	25.4	26.3	27.0	25.7	25.9	25.8	28.0	28.4	25.9	26.0	27.5
C-12 . .	20.1	21.5	21.6	21.3	21.7	21.5	21.1	22.5	22.2	22.0	22.9	20.9	22.1	22.4
C-13 . .	109.8	17.8	111.2	110.8	124.3	17.6	106.3	107.9	107.7	14.8	17.2	108.0	109.2	17.4

[a]In ppm at 75.4 MHz from $CDCl_3$ solutions.
[b]*p*-NO_2-benzoate: 164.1, 150.6, 135.7, 130.6, and 123.6.
[c]Acetate: 170.5 and 21.1.
[d]Not observed.
[e]*p*-NO_2-benzoate: 164.0, 150.6, 135.9, 130.6, and 123.6.
[f]Acetate: 170.5 and 21.2.
[g]May be interchanged.
[h]Acetate: 170.5 and 21.1.

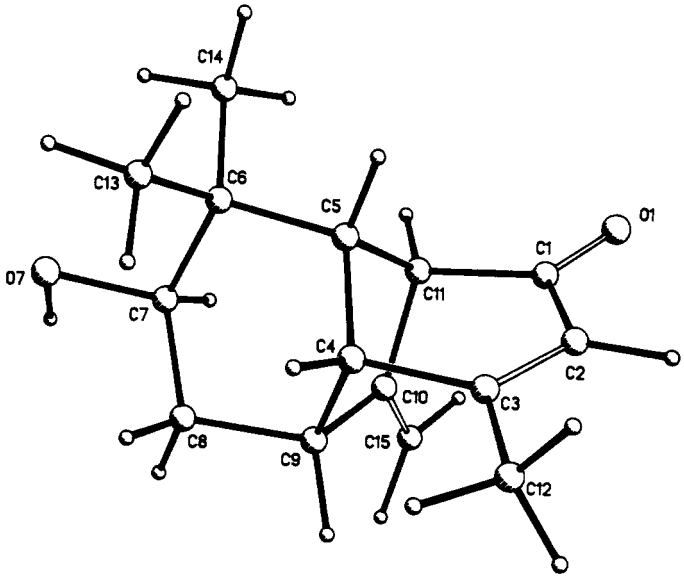

FIGURE 1. Molecular structure of dienolone **2** (atom numbering of this figure does not correspond to the formula numbering given in Scheme 1).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Organic layers were dried using anhydrous Na_2SO_4. Chromatographic separations were done using Merck Si gel 60 (70–230 mesh ASTM) or Alcoa F-20 alumina. Melting points are uncorrected. Ir spectra in $CHCl_3$ were obtained on Nicolet MX-1 or Perkin-Elmer Hitachi 599-B spectrophotometers. Specific rotations in $CHCl_3$ were determined on Perkin-Elmer 241 or 141 polarimeters. Uv spectra in EtOH were obtained on Unicam SP-800 or Perkin-Elmer Hitachi 200 spectrophotometers. The nmr measurements were performed at 300 MHz for ^1H and 75.4 MHz for ^{13}C from $CDCl_3$ solutions containing TMS as the internal standard, unless otherwise stated, on a Varian

TABLE 5. Experimentally Refined Final Fractional Atomic Coordinates ($\times 10^4$) of **2**.[a]

Atom	*x*	*y*	*z*
C-1	5703(11)	2170 (7)	3202(12)
O-1	7408 (8)	2062 (7)	3358(10)
C-2	4150(12)	1531 (8)	2005(13)
C-3	2350(12)	1632 (8)	1993(12)
C-4	1988(10)	2393 (7)	3343(11)
C-5	3763(12)	2467 (8)	5070(12)
C-6	3412(13)	3120 (8)	6566(12)
C-7	2623(15)	4278 (8)	5824(14)
O-7	1966(10)	4797 (6)	7143 (9)
C-8	1171(12)	4304 (8)	3995(13)
C-9	1809(12)	3609 (8)	2685(13)
C-10	3924(12)	3880 (7)	2996(11)
C-11	5147(12)	3059 (9)	4297(11)
C-12	659(14)	1039(10)	701(15)
C-13	1870(15)	2494 (8)	7099(14)
C-14	5286(14)	3192 (9)	8255(13)
C-15	4496(15)	4656 (8)	2163(13)

[a]Estimated standard deviations in the least significant digits are shown in parentheses.

Associates XL-300GS spectrometer. Elemental analyses were performed by the Microanalytical Laboratory Elbach, Germany. Mass spectra were recorded at 70 eV, except for compound **7**, which was recorded at 20 eV. Compound **1** was prepared by hydrolysis of the natural mixture of diesters isolated from *Stevia salicifolia* (7). This in turn allowed the preparation of **9–11** and **18** as described (7–9). Tosylate **5** was prepared in two steps (7) from rastevione [**4**] isolated from the roots of *Stevia serrata* and *Stevia rhombifolia* (13).

TREATMENT OF **1** WITH *p*-TOLUENESULFONIC ACID.—A solution of **1** (7) (300 mg) in C_6H_6 (70 ml) was treated with *p*-toluenesulfonic acid (500 mg) under reflux with a Dean-Stark trap for 2 h, concentrated, diluted with H_2O, and extracted with EtOAc. The organic layer was washed with H_2O, dried, filtered, and evaporated to dryness giving a dark oily residue which was chromatographed on alumina. The fractions eluted with hexane-C_6H_6 (1:1) afforded **3** (150 mg, 54%) as white needles. Recrystallizations from $CHCl_3$/hexane gave the analytical sample: mp 158–160°; ir ν max 1710 (C=O), 1670 and 1635 cm^{-1} (C=C-C=O); $[\alpha]_{589}$ +270°, $[\alpha]_{578}$ +284°, $[\alpha]_{546}$ +350°, $[\alpha]_{436}$ +832°, $[\alpha]_{365}$ +3370° (c = 2.00); uv λ max 239 nm (log ϵ 4.15). *Anal.* calcd for $C_{15}H_{20}O_2$: C 77.55, H 8.68, O 13.78; found C 77.44, H 8.48, O 13.74%. The fractions eluted with C_6H_6-$CHCl_3$ (3:1) provided **2** (100 mg, 36%) as white prisms. Recrystallization from $CHCl_3$/hexane afforded the pure sample: mp 130–131°; ir ν max 3605 and 3450 (OH), 1680 and 1630 (C=C-C=O), 1215 cm^{-1} (C-O); $[\alpha]_{589}$ +65°, $[\alpha]_{578}$ +68°, $[\alpha]_{546}$ +77°, $[\alpha]_{436}$ +185°, $[\alpha]_{365}$ +936° (c = 2.00); uv λ max 239 nm (log ϵ 4.64). *Anal.* calcd for $C_{15}H_{20}O_2$: C 77.55, H 8.68, O 13.78; found C 77.41, H 8.53, O 13.93%. When reflux was maintained for 6 h, only moreli-3-ene-2,7-dione [**3**] in 93% yield was obtained.

MORELI-3,9-DIEN-7β-OL-2-ONE [**2**].—A solution of **12** (50 mg) in MeOH (5 ml) was treated with KOH (50 mg) in H_2O (0.2 ml) under reflux for 1 h, concentrated, diluted with ice-H_2O, and extracted with EtOAc. The organic layer was washed with H_2O, dried, filtered, and evaporated to dryness affording **2** (26 mg, 85%) identical to **2** obtained above.

X-RAY ANALYSIS[1].—A single crystal of **2** was grown by slow crystallization from $CHCl_3$/hexane. It was monoclinic P, space group $P2_1$, with a = 7.491 (6), b = 12.136 (8), c = 8.033 (5) Å, β = 112.03 (5)°, cell volume = 676.7 (8) $Å^3$, ρ(calcd) = 1.14 g/cm^3 for Z = 2, MW 232.33, and F(000) e^- = 252. The intensity data were measured on a Nicolet R3m four-circle diffractometer equipped with CuKα radiation (λ = 1.54178 Å), operating in the θ:2θ scanning mode. The size of the crystal used was ca. 0.42 × 0.08 × 0.01 mm^3. No absorption correction was necessary (μ = 5.9 cm^{-1}). A total of 981 reflections were measured for 3°≤θ≤110°, scan width below $K_{\alpha 1}$ = 1.0 and above $K_{\alpha 2}$ = 1.2 deg, scan speed from 4.0 to 29.3 deg/min, and exposure time = 23.42 h. A total of 707 reflections were considered to be observed [$I \geq 3\sigma(I)$]. The data measured were corrected for background, Lorentz, and polarization effects, while crystal decay and absorption were negligible. The structure was solved by direct methods using the software provided by the diffractometer manufacturer. For the structural refinement the non-hydrogen atoms were treated anisotropically; the hydroxyl hydrogen became evident from a ΔF synthesis, and the hydrogen atoms bonded to carbons, included in the structure factor calculation, were refined isotropically. Final discrepancy indices were R = 6.52% using a unit weight for 596 reflections. The final difference Fourier map was essentially featureless, the highest residual peaks having densities of 0.4 e/$Å^3$. Several reflections were excluded from the final refinement calculations to improve the fit.

MORELI-3,9-DIEN-7β-OL-2-ONE *p*-NITROBENZOATE [**12**].—A solution of **9** (9) (200 mg) in C_6H_6 (20 ml) was treated with *p*-toluenesulfonic acid (130 mg) under reflux for 2 h with a Dean-Stark trap. Workup as previously gave **12** (160 mg, 84%) as white prisms. Recrystallization from $CHCl_3$/hexane gave the analytical sample: mp 217–218°; ir ν max 1725 (C=O), 1675 and 1630 (C=C-C=O), 1610 (aromatics), 1540 and 1290 cm^{-1} (NO_2); $[\alpha]_{589}$ +34°, $[\alpha]_{578}$ +41°, $[\alpha]_{546}$ +54°, $[\alpha]_{436}$ +137° (c = 1.80); uv λ max 249 (log ϵ 3.64); 210 nm (log ϵ 3.90). *Anal.* calcd for $C_{22}H_{23}O_5N$: C 69.28, H 6.08, O 20.97, N 3.67; found C 69.10, H 6.16, O 20.83, N 3.69%.

MORELI-3,9-DIEN-7β-OL-2-ONE ACETATE [**13**].—A solution of **2** (60 mg) in pyridine was treated with Ac_2O (1 ml) on a steam bath for 3 h and worked up as usual (7). The residue was crystallized from $CHCl_3$/hexane to give **13** (50 mg, 71%) as white prisms. Recrystallizations afforded the analytical sample: mp 137–139°; ir ν max 1725 (C=O, acetate), 1670 and 1625 (C=C-C=O), and 1210 cm^{-1} (C-O); $[\alpha]_{589}$ +85°, $[\alpha]_{578}$ +85°, $[\alpha]_{546}$ +104°, $[\alpha]_{436}$ +239°, $[\alpha]_{365}$ +1045° (c = 2.20); uv λ max 237 nm (log ϵ 3.94). *Anal.* calcd for $C_{17}H_{22}O_3$: C 74.42, H 8.08, O 17.49; found C 74.32, H 7.93, O 17.62%.

[1]Atomic coordinates for the structure **2** are deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

MORELI-3,9-DIENE-2,7-DIONE [**14**].—A solution of **2** (100 mg) in HOAc (1 ml) was treated with a solution of CrO_3 (100 mg) in H_2O (0.2 ml) at 0°, stored at room temperature for 1 h, poured over ice-H_2O, and extracted with Et_2O. The organic layer was washed with aqueous $NaHCO_3$ and H_2O, dried, filtered, and evaporated to dryness. The solid residue was recrystallized from $CHCl_3$/hexane to yield **14** (95 mg, 96%). Recrystallizations afforded the analytical sample as white prisms: mp 122–124°; ir ν max 1715 (C=O), 1680 and 1630 cm^{-1} (C=C-C=O); $[\alpha]_{589}$ +178°, $[\alpha]_{578}$ +182°, $[\alpha]_{546}$ +219°, $[\alpha]_{436}$ +519° (c = 2.00); uv λ max 238 nm (log ϵ 4.00). *Anal.* calcd for $C_{15}H_{18}O_2$: C 78.23, H 7.88, O 13.89; found C 78.20, H 7.20, O 14.02%.

LONGIPINENOLDIONE ACETATE [**15**].—A solution of **11** (8) (100 mg) in HOAc (2 ml) was treated as above. The solid residue was recrystallized from $CHCl_3$ to afford **15** (80 mg, 81%) as white needles. Recrystallizations provided the analytical sample: mp 186–188°; ir ν max 1740 (C=O, acetate), 1710 (C=O), 1675 and 1617 cm^{-1} (C=C-C=O); $[\alpha]_{589}$ +64°, $[\alpha]_{578}$ +68°, $[\alpha]_{546}$ +81°,$[\alpha]_{436}$ +191°, $[\alpha]_{365}$ +697° (c = 0.10); uv λ max 209 (log ϵ 3.27), 248 nm (log ϵ 3.65). *Anal.* calcd for $C_{17}H_{22}O_4$: C 70.32, H 7.64, O 22.04; found C 70.25, H 7.58, O 21.94%.

DEUTEROLONGIPINENDIOLONE [**16**].—A solution of **15** (80 mg) in MeOH (2 ml) was treated with $NaBD_4$ (10 mg) at room temperature for 1 h, poured over ice-H_2O, and extracted with EtOAc. The organic layer was washed with H_2O, dried, filtered, and evaporated to dryness. The residue was dissolved in MeOH (3 ml) and treated with KOH (40 mg) in H_2O (0.2 ml). The mixture was refluxed for 1 h. Workup as described above afforded a solid residue which was recrystallized from $CHCl_3/CCl_4$ to give **16** (25 mg, 36%) as white powder, mp 180–183°.

9-DEUTEROMORELI-3-EN-2,7-DIONE [**17**].—A solution of **16** (20 mg) in C_6H_6 (10 ml) was treated with *p*-toluenesulfonic acid (40 mg) under reflux for 9 h with a Dean-Stark trap. Workup as above afforded a dark oily residue which was chromatographed on alumina (200 mg). The fractions eluted with hexane-C_6H_6 (1:3) yielded **17** as a white solid. Recrystallizations from $CHCl_3$/hexane afforded the pure compound (10 mg, 50%) as white needles, mp 157–160°.

epi-LONGIPINANDIOLONE *p*-NITROBENZOATE [**19**].—A solution of **18** (7) (300 mg) in anhydrous pyridine (8 ml) was stirred in the presence of *p*-nitrobenzoyl chloride (300 mg) under N_2 at 4° for 24 h. Workup and chromatography as for **9** (9) yielded **19** (312 mg, 65%) as white needles. Recrystallizations from $CHCl_3$/hexane gave the analytical sample: mp 206–208°; ir ν max 3600 and 3500 (OH), 1710 (C=O), 1545 and 1280 cm^{-1} (NO_2); $[\alpha]_{589}$ −689°, $[\alpha]_{578}$ −689°, $[\alpha]_{546}$ −691°, $[\alpha]_{436}$ −691°, $[\alpha]_{365}$ −700° (c = 0.10); uv λ max 212 (log ϵ 3.81), 259 nm (log ϵ 3.35). *Anal.* calcd for $C_{22}H_{27}O_6N$: C 65.82, H 6.78, O 23.91, N 3.49; found C 65.67, H 6.71, O 23.74, N 3.56%.

epi-LONGIPINANDIOLONE ACETATE [**20**].—A solution of **10** (8) (120 mg) in MeOH (10 ml) was stirred in the presence of 5% Pd on activated charcoal (12 mg) under an H_2 atmosphere at room temperature and normal pressure until the uptake of the gas ceased. The catalyst was removed by filtration and the solvent evaporated. The residue was crystallized from CH_2Cl_2/hexane to afford **20** (85 mg, 70%) as white needles. Recrystallization afforded the pure sample: mp 146–148°; ir ν max 3595 and 3498 (OH), 1732 (C=O, acetate), 1714 cm^{-1} (C=O); $[\alpha]_{589}$ +16°, $[\alpha]_{578}$ +17°, $[\alpha]_{546}$ +18°, $[\alpha]_{436}$ +22°, $[\alpha]_{365}$ −2° (c = 0.10); ms *m/z* (rel. int.) $[M]^+$ 294.3 (1.3), 279.4 (0.5), 253.4 (0.1), 96.2 (34.6), 95.2 (24.7), 69.2 (25.0), 43.2 (100).

4-*epi*-MORELI-9-EN-7β-OL-2-ONE [**21**].—As described for **2**, reaction of **22** (100 mg) in MeOH (10 ml) with KOH (100 mg) in H_2O (0.3 ml) gave **21** (50 mg, 82%). Recrystallizations from $CHCl_3$/hexane afforded the analytical sample as white needles: mp 158–160°; ir ν max 3590 and 3390 (OH), 1700 cm^{-1} (C=O); $[\alpha]_{589}$ +80°, $[\alpha]_{578}$ +89°, $[\alpha]_{546}$ +107°, $[\alpha]_{436}$ +220°, $[\alpha]_{365}$ +507°, $[\alpha]_{334}$ +1071° (c = 2.20). *Anal.* calcd for $C_{15}H_{22}O_2$: C 76.88, H 9.46, O 13.65; found C 76.73, H 9.45, O 13.82%.

4-*epi*-MORELI-9-EN-7β-OL-2-ONE *p*-NITROBENZOATE [**22**].—As described for **12**, reaction of **19** (100 mg) in C_6H_6 (10 ml) with *p*-toluenesulfonic acid (65 mg) gave **22** (81 mg, 85%). Recrystallizations from $CHCl_3$/hexane provided the analytical sample as white needles: mp 211–213°; ir ν max 1725 (C=O's), 1545 and 1285 cm^{-1} (NO_2); $[\alpha]_{589}$ +54°, $[\alpha]_{578}$ +57°, $[\alpha]_{546}$ +66°, $[\alpha]_{436}$ +151°, $[\alpha]_{365}$ +157° (c = 0.10); uv λ max 212 (log ϵ 3.80), 256 nm (log ϵ 3.40). *Anal.* calcd for $C_{22}H_{25}O_5N$: C 68.91, H 6.57, O 20.86, N 3.65; found C 69.07, H 6.62, O 20.74, N 3.73%.

4-*epi*-MORELI-9-EN-7β-OL-2-ONE ACETATE [**23**].—As described for **12**, reaction of **20** (100 mg) in C_6H_6 (10 ml) with *p*-toluenesulfonic acid (65 mg) gave **23** (72 mg, 77%). Recrystallizations from CH_2Cl_2/hexane afforded the pure sample as white prisms: mp 78–79°; ir ν max 1733 (C=O, acetate), 1717 cm^{-1} (C=O); $[\alpha]_{589}$ +105°, $[\alpha]_{576}$ +109°, $[\alpha]_{546}$ +127°, $[\alpha]_{436}$ +268°, $[\alpha]_{365}$ +636° (c = 0.16); ms *m/z* (rel. int.) $[M]^+$ 276.2 (10.8), 261.2 (0.1), 105.2 (17.3), 91.1 (32.8), 77.1 (18.3), 43.1 (100.0).

4-*epi*-MORELIANE-2,7-DIONE [**24**].—As described for **12**, reaction of **18** (7) (350 mg) in C_6H_6 (35 ml) with *p*-toluenesulfonic acid (400 mg) gave a dark solid. Chromatography on alumina eluting with $CHCl_3$-EtOH (99:1) afforded **24** as white needles (227 mg, 70%). Recrystallizations from $CHCl_3$/hexane gave the pure sample: mp 104–105°; ir ν max 1700 cm^{-1} (C=O's); $[\alpha]_{589}$ +138°, $[\alpha]_{578}$ +142°, $[\alpha]_{546}$ +168°, $[\alpha]_{436}$ +340°, $[\alpha]_{365}$ +768° (c = 1.91). *Anal.* calcd for $C_{15}H_{22}O_2$: C 76.88, H 9.46, O 13.65; found C 76.98, H 9.50, O 13.62%.

CORRELATION OF **21** WITH **24**.—A solution of **21** (100 mg) in MeOH (3 ml) was stirred in the presence of PtO_2 catalyst (10 mg) under an H_2 atmosphere at room temperature and normal pressure until the uptake of the gas ceased. The catalyst was removed by filtration and the solvent evaporated to dryness. The residue was dissolved in HOAc (1 ml) and treated with a solution of CrO_3 (100 mg) in H_2O (0.2 ml) at 0°. The reaction mixture was stored at room temperature for 1 h and worked up as for **14**. The residue was chromatographed on Si gel eluting with hexane-EtOAc (9:1) to yield, from the first fractions, **24** (45 mg, 45%) identical to that obtained by treatment of **18** with *p*-toluenesulfonic acid. The last fractions provided *epi*-9-isomoreliane-2,7-dione [**25**] (36 mg, 36%) as a colorless oil: ir ν max 1700 cm^{-1} (C=O's); $[\alpha]_{589}$ +110°, $[\alpha]_{578}$ +115°, $[\alpha]_{546}$ +135°, $[\alpha]_{436}$ +292°, $[\alpha]_{365}$ +704° (c = 0.11); ms *m/z* (rel. int.) $[M]^+$ 234.2 (87.8), 121.1 (100.0), 91.1 (90.7), 69.0 (74.6).

LONGIPINANTRIOLONE DIACETATE TOSYLATE [**6**].—A solution of **5** (7) (1.70 g) in pyridine (10 ml) was heated on a steam bath with Ac_2O (10 ml) for 6 h. After usual workup (7), the residue was recrystallized from $CHCl_3$/hexane to provide **6** (1.33 g, 63%) as white needles. Recrystallizations afforded the pure sample: mp 225–226°; ir ν max 1750 (C=O, acetates), 1715 (C=O), 1180 cm^{-1} (S=O); $[\alpha]_{589}$ +4°, $[\alpha]_{578}$ +4°, $[\alpha]_{546}$ +3°, $[\alpha]_{436}$ −1°, $[\alpha]_{365}$ −29° (c = 0.1); uv λ max 228 (log ϵ 3.95), 262 (log ϵ 2.85), 273 (log ϵ 2.78); ms *m/z* (rel. int.) $[M]^+$ 506.5 (0.6), 466.5 (0.4), 155.2 (19.9), 109.2 (14.9), 91.2 (64.8), 43.2 (100).

ETHYLENEKETAL **7**.—A solution of **6** (900 mg) in C_6H_6 (20 ml) was treated with ethyleneglycol (10 ml) and *p*-toluenesulfonic acid (1 g) under reflux for 6 h with a Dean-Stark trap, poured over ice/aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$ and H_2O, dried, filtered, and evaporated. The solid residue was recrystallized from CH_2Cl_2/hexane to afford **7** (851 mg, 87%) as white needles: mp 114–115°; ir ν max 1745 (C=O, acetates), 1180 cm^{-1} (S=O); $[\alpha]_{589}$ +21°, $[\alpha]_{578}$ +22°, $[\alpha]_{546}$ +24°, $[\alpha]_{436}$ +36°, $[\alpha]_{365}$ +40° (c = 0.1); uv λ max 227 (log ϵ 3.99), 262 (log ϵ 2.91), 273 (log ϵ 2.82); ms *m/z* (rel. int.) $[M]^+$ 550.6 (0.1), 508.6 (0.1), 113.2 (46.8), 91.2 (16.7), 87.2 (8.2), 43.2 (100.0).

LONGIPINANDIOLONE [**26**].—A solution of **7** (500 mg) in anhydrous THF (20 ml) was slowly treated with $LiAlH_4$ (1 g) at 0°, refluxed for 2 h, cooled to 4°, treated with EtOAc and H_2O, and filtered. The organic layer was washed with H_2O, dried, filtered, and evaporated to dryness. The residue was dissolved in Me_2CO (10 ml), treated with diluted HCl (0.5 ml, 10% in H_2O), refluxed for 5 min, poured over ice, and extracted with EtOAc. The organic layer was washed with aqueous $NaHCO_3$ and H_2O, dried, filtered, and evaporated. The residue was chromatographed on Si gel. The fractions eluted with $CHCl_3$-EtOAc (6:4) provided **26** (96 mg, 42%) as white powder. Recrystallizations from Me_2CO/hexane yielded the pure compound: mp 132–133°; ir ν max 3600 and 3460 (OH), 1710 cm^{-1} (C=O); $[\alpha]_{589}$ +14°, $[\alpha]_{578}$ +14°, $[\alpha]_{546}$ +16°, $[\alpha]_{436}$ +18°, $[\alpha]_{365}$ −6° (c = 0.10); ms *m/z* (rel. int.) $[M]^+$ 252 (0.9), 238 (0.1), 55.1 (43.9), 43.1 (89.7), 41.1 (100.0), 39.1 (45.4).

ACETYLATION OF **26**.—A solution of **26** (310 mg) in CH_2Cl_2 (2 ml) was treated with acetyl chloride (0.12 ml) at room temperature for 1 h. The residue obtained after workup as above was chromatographed on Si gel. Elution with CH_2Cl_2-Me_2CO (8:2) yielded **28** (200 mg, 48%) as white needles and **27** (80 mg, 22%) as white prisms. Recrystallization of **28** from CH_2Cl_2/hexane gave the pure sample: mp 173–174°; ir ν max 1733 (C=O, acetates), 1717 cm^{-1} (C=O); $[\alpha]_{589}$ −42°, $[\alpha]_{578}$ −45°, $[\alpha]_{546}$ −51°; $[\alpha]_{436}$ −102°; $[\alpha]_{365}$ −209° (c = 0.16); ms *m/z* (rel. int.) $[M]^+$ 336.4 (0.4), 294.3 (0.5), 95.2 (11.1), 55.1 (9.4), 43.1 (100.0), 41.2 (13.9). Recrystallizations of **27** from CH_2Cl_2/hexane afforded the pure compound: mp 119–120°; ir ν max 3620 and 3452 (OH), 1735 (C=O, acetate), 1720 cm^{-1} (C=O); $[\alpha]_{589}$ 0°, $[\alpha]_{578}$ 0°, $[\alpha]_{546}$ 0°, $[\alpha]_{436}$ −2°, $[\alpha]_{365}$ −29° (c = 0.10); ms *m/z* (rel. int.) $[M]^+$ 294.2 (0.4), 252.2 (0.1), 69.1 (25.2), 55.1 (30.1), 43.1 (100.0), 41.1 (27.6).

TREATMENT OF **26** WITH *p*-TOLUENESULFONIC ACID.—As described for **1**, reaction of **26** (500 mg) in C_6H_6 (28 ml) with *p*-toluenesulfonic acid (140 mg) under reflux for 1 h gave a yellow oily residue which was chromatographed on Si gel. Elution with CH_2Cl_2-Me_2CO (8:2) yielded from the first fractions **31** (130 mg, 28%) as a colorless oil: ir ν max 1710 cm^{-1} (C=O's); $[\alpha]_{589}$ +72°, $[\alpha]_{578}$ +76°, $[\alpha]_{546}$ +89°, $[\alpha]_{436}$ +179°, $[\alpha]_{365}$ +390° (c = 0.42); ms *m/z* (rel. int.) $[M]^+$ 234.2 (6.7), 221.3 (0.2), 43.2 (53.4), 42.2 (62.3), 41.1 (100.0), 39.1 (55.7). The last fractions provided **29** (220 mg, 40%) as a white

powder. Recrystallizations from CH_2Cl_2/hexane gave the pure sample: mp 100–102°; ir ν max 3600 and 3480 (OH), 1710 cm^{-1} (C=O); $[\alpha]_{589}$ +88°, $[\alpha]_{578}$ +91°, $[\alpha]_{546}$ +106°, $[\alpha]_{436}$ +205°, $[\alpha]_{365}$ +420° (c = 0.10); ms *m/z* (rel. int.) $[M]^+$ 234.1 (35.4), 232.2 (0.2), 149.1 (100.0), 121.1 (48.4), 107.1 (58.2), 91.1 (84.1).

MORELI-9-EN-7β-OL-2-ONE ACETATE [**30**].—As described for **12**, reaction of **27** (53 mg) in C_6H_6 (8 ml) with *p*-toluenesulfonic acid (100 mg) afforded **30** (40 mg, 80%) as white needles. Recrystallizations from CH_2Cl_2/hexane gave the pure compound: mp 99–101°; ir ν max 1732 (C=O, acetate), 1717 cm^{-1} (C=O); $[\alpha]_{589}$ +44°, $[\alpha]_{578}$ +46°, $[\alpha]_{546}$ +53°, $[\alpha]_{436}$ +100°, $[\alpha]_{365}$ +189° (c = 0.14); ms *m/z* (rel. int.) $[M]^+$ 276.2 (4.0), 105.2 (19.9), 91.2 (17.7), 77.2 (13.9), 43.1 (100.0).

HYDROGENATION OF **2**.—As described for **20**, a solution of **2** (200 mg) in EtOAc (10 ml) with 5% Pd over charcoal catalyst (20 mg) afforded a mixture of **21** and **29** in ca. 1:1 ratio as judged by ^1H nmr. The mixture was separated by cc on Si gel, eluting with hexane-EtOAc (9:1) to yield **21** (86 mg, 85%) and **29** (79 mg, 78%).

HYDROGENATION OF **3**.—As described for **20**, a solution of **3** (150 mg) in EtOAc (8 ml) with 5% Pd over charcoal catalyst (15 mg) afforded **24** (137 mg, 91%).

KINETIC MEASUREMENTS.—A mixture of *p*-toluenesulfonic acid monohydrate (120 mg, 0.63 mM) in C_6D_6-C_6H_6 (4:6) (10 ml) was refluxed for 30 min. Once the *p*-toluenesulfonic acid dissolved, 0.22 mM of the corresponding compound (**2**, **10**, **20**, **21**, **27**, or **29**) was added. Aliquots of 1 ml were withdrawn from the reaction mixtures, each 15 min during the first hour and each 30 min during the subsequent 3 h. The aliquots were cooled at 0° immediately after withdrawal. The changes in molar composition of the reaction mixtures were evaluated from integrals of the vinylic protons and/or the tertiary methyl groups found in the 300 MHz ^1H-nmr spectra. The relative rate constants for each transformation were estimated by least-squares plots of the natural logarithm of the starting material molar concentration vs. time.

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