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MOLECULAR REARRANGEMENT OF RASTEVIONE MESYLATE INTO ARTEAGANE DERIVATIVES

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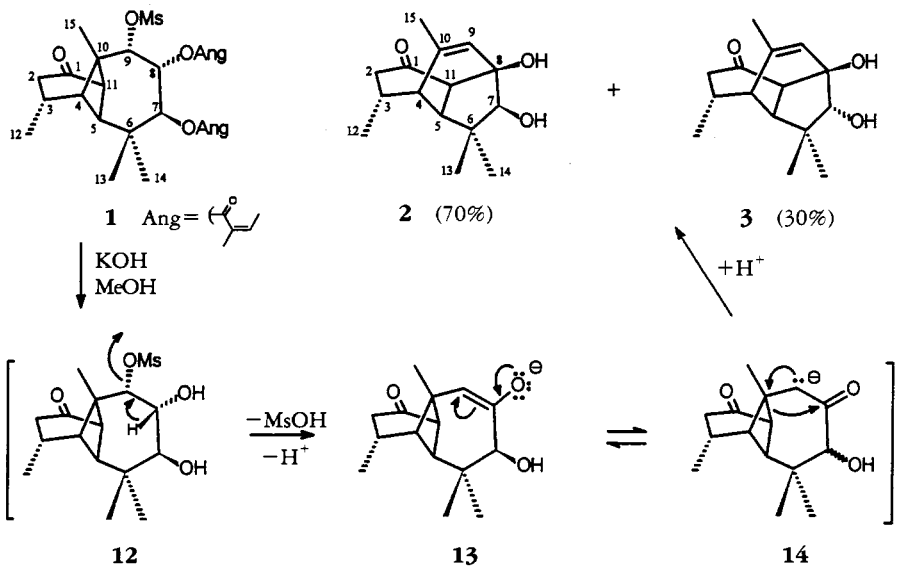
ABSTRACT.—Molecular rearrangment of rastevione mesylate [**1**] in alkaline medium afforded two epimeric 2,6,6,11-tetramethyltricyclo[5.4.0.0^{4,8}]undecane derivatives [**2** and **3**] by a 1,3-bond migration. Their stereostructures, which possess a new hydrocarbon skeleton named arteagane, were elucidated from nmr data in combination with X-ray diffraction analyses of **3** and its diacetate **7**. The conformations of **2**, **3**, and several derivatives are reported.

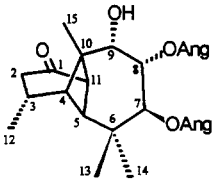
Molecular rearrangements of natural products offer the possibility of generating substances with novel skeletons (1–3) and increased understanding of their chemical behavior (4–6), which can be applied to synthetic approaches (7,8). In continuation of our research on molecular rearrangements of sesquiterpenes (9,10), we report herein the transformation of the longipinene derivative rastevione mesylate [**1**] to the 2,6,6,11-tetramethyltricyclo[5.4.0.0^{4,8}]undecane derivatives **2** and **3** by a 1,3-bond migration. The new hydrocarbon skeleton generated has been named arteagane.

RESULTS AND DISCUSSION

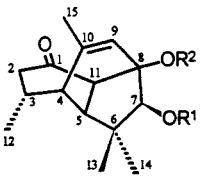
Rastevione [**4**] was obtained in high yields from the roots of *Stevia serrata* Cav. (Asteraceae) (11). Its treatment with methanesulfonyl chloride in pyridine afforded **1** which, upon treatment with KOH in MeOH, reacted to give **2** and **3** (Scheme 1) in a



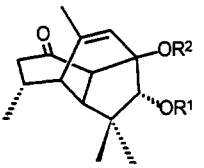
SCHEME 1. Proposed pathways for the transformation of rastevione mesylate [**1**] into the 2,6,6,11-tetramethyltricyclo[5.4.0.0^{4,8}]undecane (arteagane) derivatives **2** and **3**.



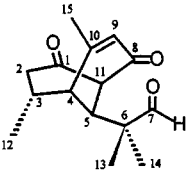
4 Ang= 



5 $R^1=R^2=Ac$
6 $R^1=Ac$; $R^2=H$



7 $R^1=R^2=Ac$
8 $R^1=Ac$; $R^2=H$



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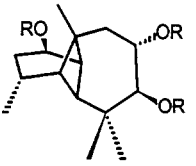

10 R=H
11 R=Ac

7:3 ratio as shown by ^{1}H-nmr analysis. Both substances showed the same number of ^{1}H- (Table 1) and ^{13}C-nmr (Table 2) signals and multiplicities, but exhibited differences in chemical shift values. This suggested that both compounds had the same structure but different stereochemistries. Also, both substances showed ir bands indicative of hydroxyl and keto groups. Their ^{1}H-nmr spectra showed signals for a vinylic proton, a proton geminal to an oxygen as a sharp singlet, two broad signals which exchanged in the presence of D_2O, a vinylic methyl group, two tertiary methyl groups, and one secondary methyl group.

The presence of one secondary hydroxyl group and one tertiary hydroxyl group in **2** was evident after treatment with Ac_2O in pyridine for 90 min on a steam bath, since a mixture of diacetate **5** and monoacetate **6** was obtained. Diacetate **5** showed ^{1}H-nmr signals for the acetyl groups at 2.09 and 1.99 ppm, and for H-7 at 5.01 ppm, while monoacetate **6** showed signals for the acetyl group at 2.11 and H-7 at 4.54 ppm, respectively, and for the exchangeable proton OH-8 at 2.68 ppm. When the reaction time was increased from 90 min to 6 h, only diacetate **5** was obtained. By the same procedure, **3** led to diacetate **7** and monoacetate **8**. Furthermore, when **2** or **3** was treated with periodic acid in THF, to oxidize the 1,2-diol moiety, the expected diketoaldehyde **9** was obtained. Alternatively, treatment of mesylate **1** with $LiAlH_4$ afforded triol **10** as the only product, which was fully characterized as its triacetate **11**.

The ^{1}H- and ^{13}C-nmr spectra summarized in Tables 1 and 2, respectively, were assigned by HETCOR experiments carried out for each substance. The ^{13}C-nmr *gem*-dimethyl group signals of **3** and **5–8** were assigned individually by considering the effects due to stereochemical changes of OH and OAc groups in five-membered rings, as in ring-D functionalized steroids (12).

To support the structures of the rearranged products **2**, **3**, and **5–8**, since they possess the new hydrocarbon skeleton, 2,6,6,11-tetramethyltricyclo[5.4.0.0^{4,8}]undecane, which we have named arteagane, it was desirable to perform the X-ray diffraction analysis of at least one of these substances. Diolenone **3** as well as diacetate **7** provided suitable crystals for this purpose. The perspective views of the molecular structures are shown in Figures 1 and 2 and the experimentally refined final fractional atomic coordinates are listed in Table 3. In the solid state, the conformation of the C-1–C-2–C-3–C-4–C-5–C-11 ring (A) is quite similar in the two substances (**3** and **7**) as shown

TABLE 1. ^{1}H-Nmr Chemical Shifts (Multiplicities and Coupling Constants in Hz) for Compounds **1–3**, **5–9**, and **11**.[a]

Proton	Compound								
	1[b]	**2**[c]	**3**[d]	**5**[e]	**6**[f]	**7**[g]	**8**[h]	**9**	**11**[i]
H-1	—	—	—	—	—	—	—	—	5.14 (m)
H-2α	2.16 (dd, 19,6)	2.03 (dd, 16,4)	2.05 (dd, 16,4)	2.14 (dq, 16,1)	2.10 (dd, 17,3)	2.12 (dq, 15,1)	2.06 (dd, 16,5)	2.17 (qd, 16,1)	1.78–1.86 (m)
H-2β	2.62 (dd, 19,9)	2.44 (dd, 16,7)	2.45 (dd, 16,8)	2.79 (dd, 16,7)	2.46 (dd, 17,8)	2.98 (dd, 15,7)	2.46 (dd, 16,8)	2.74 (dd, 16,8)	1.78–1.86 (m)
H-3	2.39 (m)	2.18 (m)	2.17 (m)	2.41 (m)	2.28 (m)	2.44 (m)	2.16 (m)	2.41 (m)	2.35 (m)
H-4	2.36 (br d, 6)	1.92 (m)	2.01 (m)	2.01 (m)	2.02 (m)	2.02 (m)	2.01 (m)	2.34 (m)	1.96 (br d, 5)
H-5	1.87 (br s)	2.09 (dd, 6,4)	2.19 (dd, 5,3)	2.21 (dd, 6,3)	2.17 (dd, 6,3)	2.24 (dd, 5,3)	2.22 (dd, 6,3)	2.63 (t, 2)	1.24 (br s)
H-7	5.46 (d, 11)	3.36 (s)	3.63 (s)	5.01 (s)	4.54 (s)	4.92 (s)	4.69 (s)	9.33 (s)	4.97 (d, 11)
H-8	5.51 (dd, 11,2)	—	—	—	—	—	—	—	5.17 (td, 11,5)
H-9	5.02 (d, 2)	5.44 (quint., 1)	5.44 (quint., 1)	5.66 (quint., 1)	5.48 (quint., 1)	5.42 (quint., 1)	5.42 (quint., 1)	6.02 (quint., 1)	1.72 (dd, 14,11)[j] 1.93 (dd, 14,5)[k]
H-11	3.03 (d, 6)	2.78 (br d, 6)	2.62 (br d, 5)	3.01 (br d, 5)	2.80 (br d, 6)	2.99 (br d, 5)	2.68 (br d, 6)	3.51 (br s)	2.28 (br t, 5)
CH_3-12	1.13 (d, 7)	1.07 (d, 7)	1.09 (d, 7)	1.06 (d, 7)	1.10 (d, 7)	1.01 (d, 7)	1.03 (d, 7)	1.26 (d, 7)	0.94 (d, 7)
CH_3-13	1.12 (s)	1.04 (s)[l]	1.13 (s)	0.97 (s)	0.96 (s)	1.25 (s)	1.26 (s)	1.09 (s)[l]	0.98 (s)
CH_3-14	0.97 (s)	1.05 (s)[l]	0.94 (s)	1.19 (s)	1.17 (s)	0.86 (s)	0.85 (s)	1.08 (s)[l]	0.92 (s)
CH_3-15	1.11 (s)	1.65 (d, 1)	1.72 (d, 1)	1.77 (d, 1)	1.74 (d, 1)	1.80 (d, 1)	1.70 (d, 1)	2.06 (d, 1)	1.06 (s)

[a]Measured at 300 MHz from $CDCl_3$ solutions using TMS as internal standard.
[b]AngO: 6.15 and 6.11 (qq, 7,2); 1.99 and 1.98 (dq, 7,2); 1.87 and 1.78 ppm (quint., 2). MsO: 3.21 ppm (s).
[c]OH: 3.80 (br s) and 3.35 ppm (br s).
[d]OH: 3.48 (br s) and 2.40 ppm (br s).
[e]AcO: 2.09 (s) and 1.99 ppm (s).
[f]OH: 2.68 ppm (s). AcO: 2.11 ppm (s).
[g]AcO: 2.11 (s) and 1.99 ppm (s).
[h]OH: 3.35 ppm (s). AcO: 2.01 ppm (s).
[i]AcO: 2.06 (s), 2.01 (s) and 2.00 ppm (s).
[j]H-9α.
[k]H-9β.
[l]May be interchanged.

TABLE 2. ^{13}C-Nmr Chemical Shifts for Compounds **1–3**, **5–9**, and **11**.[a]

Carbon	Compound								
	1[b]	**2**	**3**	**5**[c]	**6**[d]	**7**[e]	**8**[f]	**9**	**11**[g]
C-1	210.0	215.2	214.3	210.1	212.2	209.3	213.8	201.3	75.5
C-2	41.6	44.3	44.5	43.9	43.9	44.1	44.6	42.6	32.9
C-3	26.9	28.9	29.1	31.2	29.3	31.9	28.9	32.5	30.1
C-4	44.9	44.1	44.6	43.3	43.5	43.9	44.8	43.5	45.0
C-5	46.3	46.3	45.3	47.5	46.4	47.9	45.8	46.3	48.8
C-6	35.1	41.7	38.4	42.0	42.0	38.3	38.9	48.1	34.7
C-7	70.2	81.7	87.0	81.2	82.9	85.9	88.2	203.4	77.4
C-8	68.9	80.8	82.1	84.9	79.8	86.2	80.3	191.7	69.6
C-9	84.4	129.1	127.4	124.6	127.7	124.7	128.6	126.8	44.1
C-10 ...	45.8	137.5	136.8	138.3	138.2	134.6	135.3	164.2	38.8
C-11 ...	52.2	53.7	52.5	55.2	55.8	53.1	52.0	63.6	44.6
C-12 ...	19.6	21.3	20.9	19.5	20.5	19.2	21.4	20.7	20.9
C-13 ...	20.0	26.0[h]	32.6[i]	26.1[i]	26.1[i]	31.6[i]	31.9[i]	21.7[h]	20.0
C-14 ...	26.7	25.9[h]	19.7[i]	25.3[i]	25.3[i]	19.7[i]	19.8[i]	21.0[h]	27.7
C-15 ...	20.0	19.8	19.9	19.8	19.7	19.9	19.8	23.3	23.5

[a]Measured at 75.4 MHz from $CDCl_3$ solutions using TMS as internal standard.
[b]AngO: 166.6, 166.4, 140.7, 140.2, 127.2, 126.7, 20.6, 19.9, 15.9, and 15.7 ppm. MsO: 39.3 ppm.
[c]AcO: 170.0, 169.6, 21.3, and 20.7 ppm.
[d]AcO: 170.4 and 20.5 ppm.
[e]AcO: 170.7, 170.1, 21.4, and 20.9 ppm.
[f]AcO: 171.4 and 20.9 ppm.
[g]AcO: 170.5, 170.2, 170.0, 21.4, 21.0, and 20.8 ppm.
[h]May be interchanged.
[i]Assignments made considering the effects of stereochemical changes of OH and OAc groups in steroids [see Cerda-García-Rojas *et al.* (15)].

in Figures 1 and 2 and as indicated from the H-2α–C-2–C-3–H-3 torsion angles which are −77.9° (0.1) for **3** and −74.5° (0.1) for **7**. In contrast, the ^{1}H-nmr spectra of **2**, **3**, and **5–8** show that $J_{2\alpha,3}$ varies significantly from 1.4 to 5.0 Hz, while $J_{2\beta,3}$ remains essentially unchanged, as shown in Table 1. These values rule out the preference of a single conformation, since they can be attributed to coupling constant averages arising from conformational equilibria. Molecular models of arteaganes **2**, **3**, **5–8** were generated using the PCMODEL program. In all cases two energetic minima were found, which correspond to two different conformations of ring A, as shown for **2** in Figure 3.

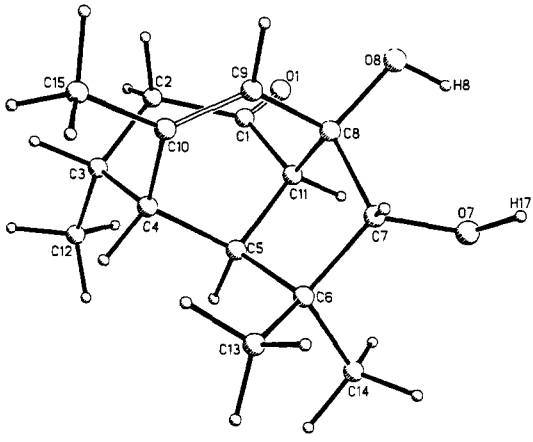

FIGURE 1. X-ray structure of diolenone **3**.

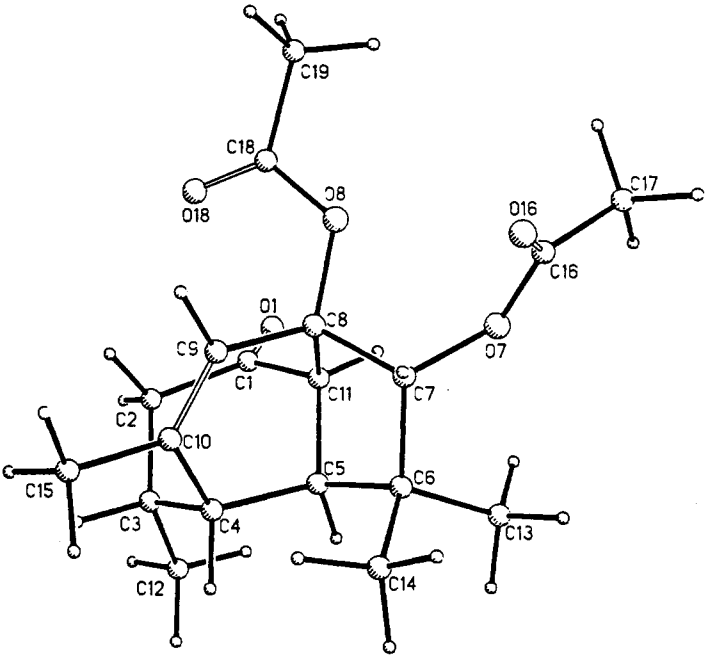

FIGURE 2. X-ray structure of diacetate **7**.

TABLE 3. Experimentally Refined Final Fractional Atomic Coordinates ($\times 10^4$) of **3** and **7**.[a]

Atom	Compound					
	3			**7**		
	x	*y*	*z*	*x*	*y*	*z*
C-1	4006 (3)	814 (2)	3693 (2)	445 (4)	1408 (3)	7671 (3)
O-1	5182 (3)	1313 (2)	4058 (1)	−294 (3)	1887 (2)	8174 (3)
C-2	4170 (4)	463 (2)	2731 (2)	488 (4)	155 (3)	7662 (3)
C-3	3139 (4)	−611 (2)	2477 (2)	535 (4)	−311 (3)	6588 (3)
C-4	1326 (4)	−552 (2)	2894 (2)	1487 (3)	309 (3)	5984 (3)
C-5	1457 (3)	−561 (2)	3919 (2)	1189 (3)	1546 (3)	5900 (2)
C-6	−269 (3)	−501 (2)	4453 (2)	2068 (3)	2310 (3)	5316 (2)
C-7	−616 (4)	810 (2)	4592 (2)	2939 (3)	2742 (3)	6122 (3)
O-7	−524 (3)	1145 (2)	5505 (1)	2743 (2)	3929 (2)	6311 (2)
C-8	865 (3)	1389 (2)	4056 (2)	2582 (3)	2101 (3)	7064 (3)
O-8	1242 (3)	2522 (1)	4337 (1)	3023 (2)	2744 (2)	7891 (2)
C-9	303 (4)	1406 (2)	3093 (2)	3146 (3)	958 (3)	7010 (3)
C-10	415 (4)	509 (2)	2571 (2)	2693 (4)	152 (3)	6489 (3)
C-11	2376 (3)	549 (2)	4199 (2)	1211 (3)	2039 (3)	6958 (2)
C-12	4129 (4)	−1697 (2)	2716 (2)	−697 (4)	−292 (4)	6104 (3)
C-13	−1794 (4)	−1052 (3)	3972 (2)	1359 (4)	3261 (4)	4833 (3)
C-14	−7 (4)	−1110 (3)	5344 (2)	2774 (4)	1687 (4)	4498 (3)
C-15	−283 (5)	482 (3)	1621 (2)	3269 (5)	−984 (5)	6409 (4)
C-16				3692 (3)	4553 (4)	6534 (3)
O-16				4695 (3)	4234 (3)	6461 (3)
C-17				3321 (4)	5686 (3)	6853 (4)
C-18				2934 (4)	2313 (4)	8798 (3)
O-18				2415 (4)	1471 (3)	8989 (2)
C-19				3567 (4)	3040 (4)	9567 (3)

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

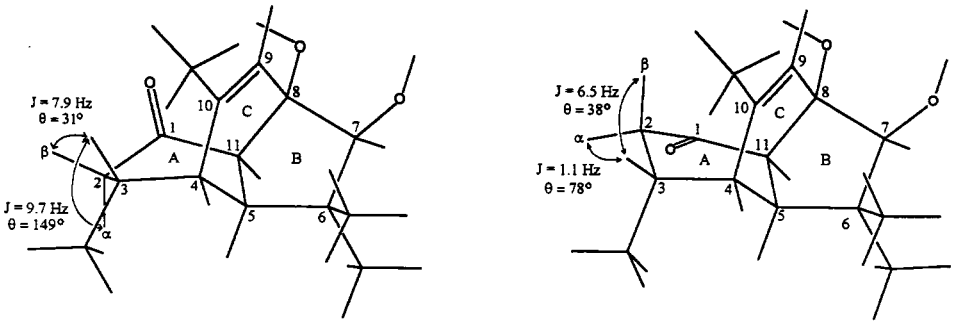

FIGURE 3. MMX molecular models of **2** showing the two preferred conformations (**a** and **b**) in solution.

Therefore, for structure **a**, ring A exists in a conformation midway between boat and half-chair, where the methyl group at C-3 has a quasi-equatorial orientation, while in structure **b** this ring adopts a conformation midway between chair and half-chair, where the methyl group at C-3 has a quasi-axial orientation. In order to determine the conformer population in solution, we employed the equation of Eliel (13) in the form

TABLE 4. Crystal Data of the 2,6,6,11-Tetramethyltricyclo[5.4.0.$0^{4,8}$]undecane Derivatives **3** and **7**.

Parameters and Refinement	Compound	
	3	**7**
Crystal Parameters		
Chemical formula	$C_{15}H_{22}O_3$	$C_{19}H_{26}O_5$
Molecular weight	250.3408	334.4161
Crystal system	orthorombic	orthorombic P
Space group	$P2_12_12_1$	$P2_12_12_1$
Crystal size, mm	0.40×0.14×0.08	0.50×0.25×0.10
Crystal color	white	white
Cell constants		
a, Å	7.806 (3)	11.240 (4)
b, Å	11.747 (5)	12.062 (5)
c, Å	15.031 (6)	13.506 (7)
Cell volume, Å^3	1378.2 (10)	1831.0 (14)
ρ(calcd), g/cm^3	1.20	1.21
Z	4	4
F(000), e$^-$	528	720
Data Collection Parameters		
μ, cm^{-1}	6.25	7.20
Scan width, below $K_{\alpha 1}$, above $K_{\alpha 2}$, deg	1.0–1.0	0.8–1.0
2θ limits, deg	3–110	3–110
Scan speed, deg min^{-1}	variable, 4–29	variable, 4–29
Exposure time, h	19.00	27.70
Reflections collected	1047	1363
Observed reflections	967	1319
Structure Refinement		
Reflections for final refinement	942	1299
Parameters refined	183	231
R(F), %	3.52	5.32
R_w(F), %	3.96	6.08
Goodness of fit for the last cycle	1.151	1.136
Final G	0.00185	0.00417
Δ_e (e/Å^3)	0.1339	0.3440

$K_{a/b}=(J_a-J_{obs})/(J_{obs}-J_b)$, where J_a (9.7 Hz) and J_b (1.1 Hz) are the calculated coupling constants $J_{2\alpha,3}$ for conformers **a** and **b**, respectively (see Figure 3). They were obtained by introducing the dihedral angles H-2α–C-2–C-3–H-3 obtained from the MMX molecular models of arteaganes into the equation of Altona (14,15). J_{obs} is the observed $J_{2\alpha,3}$ for each compound. The results, summarized in Table 5, show that the equilibria are important in alcohols **2** and **3** and monoacetates **6** and **8**, while diacetates **5** and **7** exist mainly in conformation **b**. This fact can be attributed to the steric effect between the acetyl group at C-8 and the oxygen atom of the carbonyl group at C-1. Preference of diacetates **5** and **7** for conformation **b** is further evidenced by the long-range coupling constants among H-2a, H-4, and H-11 (see Table 1), which in this conformation are in a *W*-type arrangement. The ^{13}C-nmr data are also consistent with the values given in Table 4. For example, the signal for C-12 shows a variation from 19.2 ppm in **7**, where this methyl group remains essentially quasi-equatorial, to 21.4 ppm in **8** where an almost equimolar proportion of quasi-equatorial and quasi-axial orientations of C-12 exists. Conformations **a** and **b** are close to those we found in a 4,8,8-trimethyl-9-methyleneperhydro-1,5-methanonaphthalene derivative (16) and conformation **b** is very similar to that found for both **3** and **7** in the solid state.

Finally, from the mechanistic point of view we propose the pathway drawn in Scheme 1 for the transformation of **1** to **2** and **3**. Hydrolysis of the angeloyl esters leads to intermediate **12**, which undergoes a mesylate elimination to afford **13** followed by tautomerization to ketone **14** and final 1,3-transposition of the C-11–C-10 bond, with assistance of the anion at C-9 to form the C-11–C-8 bond. The fact that the chiral center at C-7 is partially isomerized supports the presence of a carbonyl group at C-8, as in **14**, during the reaction path.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Organic layers were dried using anhydrous Na_2SO_4. Chromatographic separations were performed using Merck Si gel 60 (230–400 mesh ASTM). Mps are uncorrected. Ir spectra in $CHCl_3$ were determined on a Nicolet MX-1 or Perkin-Elmer 599B spectrophotometer. Optical rotations in $CHCl_3$ were determined on a Perkin-Elmer 141 polarimeter. Uv spectra were recorded on a Hitachi 200 spectrophotometer. Nmr measurements were done using a Varian Associates XL-300GS spectrometer from $CDCl_3$ solutions containing TMS as the internal standard. The ^{1}H-nmr spectra were run at 300 MHz (see Table 1) and the ^{13}C-nmr spectra at 75.4 MHz (see Table 2). Elemental analyses were performed by the Microanalytical Laboratory, Elbach, Germany.

Rastevione mesylate [**1**].—A solution of rastevione [**4**] isolated from *Stevia serrata* (11) (2 g) in pyridine (6 ml) was treated with methanesulfonyl chloride (0.35 ml) at 0°. The reaction mixture was stored at room temperature for 24 h, poured over ice, and extracted with EtOAc. The organic layer was washed with dilute HCl, H_2O, aqueous $NaHCO_3$, and H_2O, dried, filtered, and evaporated. The residue was crystallized from CH_2Cl_2-hexane to afford **1** (1.92 g, 81%) as white flakes, mp 170–172°; $[\alpha]_{589}$ −41°, $[\alpha]_{578}$ −42°, $[\alpha]_{546}$ −49°, $[\alpha]_{436}$ −89°, $[\alpha]_{365}$ −181°, $[\alpha]_{334}$ −339° (*c*=2.0, $CHCl_3$); ir (film) ν max 1712, 1210, 1176, 1158

TABLE 5. Observed $J_{2\alpha,3}$ in Arteagane Derivatives **2**, **3**, and **5–8**, $K_{a/b}$ and the Conformational Population in Solution.

Compound	$J_{2\alpha,3}$ (Hz)	$K_{a/b}$	Conformational population (%)	
			Conformer **a**	Conformer **b**
2	4.4	0.61	38	62
3	4.0	0.52	34	66
5	1.4	0.03	3	97
6	2.5	0.19	16	84
7	1.4	0.03	3	97
8	5.0	0.82	45	55

cm^{-1}, uv (MeOH) λ max (log ε) 218 (4.35) nm; *anal.*, calcd for $C_{26}H_{38}O_8S$, C 61.16, H 7.50, O 25.07, S 6.27; found C 61.02, H 7.38, O 25.18, S 6.43%.

Arteag-9-en-7β,8β-diol-1-one [**2**] *and arteag-9-en-7α,8β-diol-1-one* [**3**].—A solution of rastevione mesylate [**1**] (500 mg) in MeOH (20 ml) was treated with a solution of KOH (500 mg) in H_2O (0.7 ml). The reaction mixture was refluxed for 30 min, concentrated to one-half, poured over ice, and extracted with EtOAc. The organic layer was washed with H_2O, dried, filtered, and evaporated. The residue was chromatographed (SiO_2) eluting with hexane-EtOAc (8:2). The first fractions yielded **2** as a white solid which was recrystallized from CH_2Cl_2/hexane to afford white prisms (142 mg, 58%), mp 139–141°; $[\alpha]_{589}$ +15°, $[\alpha]_{578}$ +15°, $[\alpha]_{546}$ +18°, $[\alpha]_{436}$ +54°, $[\alpha]_{365}$ +210°, $[\alpha]_{334}$ +622° (*c*=2.0, $CHCl_3$); ir ($CHCl_3$) ν max 3500, 1690 cm^{-1}; *anal.*, calcd for $C_{15}H_{22}O_3$, C 71.97, H 8.86, O 19.17; found C 71.98, H 8.47, O 19.33%. The last fractions afforded **3** as a white solid which was recrystallized from CH_2Cl_2/hexane to afford white prisms (51 mg, 21%); mp 104–106°; $[\alpha]_{589}$ −74°, $[\alpha]_{578}$ −78°, $[\alpha]_{546}$ −91°, $[\alpha]_{436}$ −138°, $[\alpha]_{365}$ −141° (*c*=0.09, $CHCl_3$); ir ($CHCl_3$) ν max 3584, 3440 cm^{-1}.

Arteag-9-en-7β,8β-diol-1-one 7,8-diacetate [**5**].—A solution of **2** (130 mg) in pyridine (3 ml) was treated with Ac_2O (3 ml). The reaction mixture was heated on a steam bath for 6 h, poured over ice H_2O, and extracted with EtOAc. Workup as in the case of **1** gave a residue which was purified by cc over Si gel. The fractions eluted with hexane/EtOAc yielded diacetate **5** as a white solid which was recrystallized from $CHCl_3$/hexane to afford white prisms (128 mg, 74%), mp 171–173°; $[\alpha]_{589}$ −29°, $[\alpha]_{578}$ −32°, $[\alpha]_{546}$ −32°, $[\alpha]_{436}$ −61°, $[\alpha]_{365}$ −117°, $[\alpha]_{334}$ −228° (*c*=2.0, $CHCl_3$); ir ($CHCl_3$) ν max 1740, 1695 cm^{-1}; *anal.*, calcd for $C_{19}H_{26}O_5$, C 68.24, H 7.84, O 23.92; found C 68.23, H 7.88, O 23.91%.

Arteag-9-en-7β,8β-diol-1-one 7-monoacetate [**6**].—A solution of endiolone **2** (100 mg) in pyridine (1.5 ml) was treated with Ac_2O (1.5 ml). The reaction mixture was heated on a steam bath for 90 min, poured over ice-H_2O, and extracted with EtOAc. Workup as for **1** gave a residue which was chromatographed over Si gel. The fractions eluted with C_6H_6-$CHCl_3$ (1:1) afforded diacetate **5** (45 mg, 34%) identical to that described above and the fractions eluted with $CHCl_3$ gave monoacetate **6** which was recrystallized from CH_2Cl_2/hexane to yield white prisms (27 mg, 23%), mp 109–111°; $[\alpha]_{589}$ −40°, $[\alpha]_{578}$ −50°, $[\alpha]_{546}$ −54°, $[\alpha]_{436}$ −59°, $[\alpha]_{365}$ −21°, $[\alpha]_{334}$ +222° (*c*=2.0, $CHCl_3$); ir ($CHCl_3$) ν max 3520, 1740 cm^{-1}.

Arteag-9-en-7α,8β-diol-1-one 7,8-diacetate [**7**].—A solution of **3** (100 mg) in pyridine (3 ml) was treated with Ac_2O (3 ml). The reaction mixture was heated on a steam bath for 6 h, poured over ice-H_2O, and extracted with EtOAc. Workup as in the case of **1** gave a residue which was purified by cc over Si gel. The fractions eluted with hexane-EtOAc (8:2) afforded diacetate **7** as a white solid which was recrystallized from $CHCl_3$/hexane to yield white prisms (97 mg, 73%), mp 128–130°; $[\alpha]_{589}$ −40°, $[\alpha]_{578}$ −42°, $[\alpha]_{546}$ −49°, $[\alpha]_{436}$ −95°, $[\alpha]_{365}$ −196° (*c*=3.1, $CHCl_3$); ir ($CHCl_3$) ν max 1730, 1696 cm^{-1}.

Arteag-9-en-7α,8β-diol-1-one 7-monoacetate [**8**].—A solution of endiolone **3** (83 mg) in pyridine (1 ml) was treated with Ac_2O (1 ml). The reaction mixture was heated on a steam bath for 90 min, poured over ice-H_2O, and extracted with EtOAc. Workup as in the case of **1** gave a residue which was chromatographed over Si gel. The first fractions eluted with hexane-EtOAc (8:2) afforded diacetate **7** (35 mg, 32%) identical to that described above and the fractions following eluted with the same solvent gave monoacetate **8** (17 mg, 18%) as a white solid mp 102–103°; $[\alpha]_{589}$ −73°, $[\alpha]_{578}$ −77°, $[\alpha]_{546}$ −88°, $[\alpha]_{436}$ −147°, $[\alpha]_{365}$ −201° (*c*=1.3, $CHCl_3$); ir ($CHCl_3$) ν max 3524, 1730, 1708 cm^{-1}.

Diketoaldehyde [**9**].—A solution of **2** or **3** or a mixture of both (100 mg) in THF (3 ml) was treated with a solution of periodic acid (200 mg) in H_2O (0.5 ml). The reaction mixture was stirred at 0° for 90 min, poured over ice, and extracted with EtOAc. The organic layer was washed with H_2O, dried, filtered and evaporated giving **9** (84 mg, 85%) as a white solid, mp 71–73°; $[\alpha]_{589}$ +301°, $[\alpha]_{578}$ +325°, $[\alpha]_{546}$ +385°, $[\alpha]_{436}$ +895°, $[\alpha]_{365}$ +2073° (*c*=2.0, $CHCl_3$); ir ($CHCl_3$) ν max 1720, 1660 cm^{-1}.

Longipinan-1β,7β,8α-triol [**10**].—A solution of mesylate **1** (500 mg) in anhydrous THF (40 ml) was slowly treated with $LiAlH_4$ (1 g) at 0°, refluxed for 2 h, evaporated to one third, cooled to 0°, treated with EtOAc, MeOH, and H_2O, and filtered. The organic layer was washed with H_2O, dried, filtered and evaporated to dryness giving **10** (200 mg, 80%) as a colorless oil: ir ($CHCl_3$) ν max 3600, 3400 cm^{-1}.

Longipinan-1β,7β,8α-triol 1,7,8-triacetate [**11**].—A solution of **10** (100 mg) in pyridine (1 ml) was treated with Ac_2O (1 ml). The reaction mixture was heated on a steam bath for 2 h, poured over ice-H_2O, and extracted with EtOAc. Workup as for **1** gave triacetate **11** as a solid residue which was recrystallized from $CHCl_3$/hexane to afford white needles (90 mg, 60%), mp 210–212°; $[\alpha]_{589}$ −2°, $[\alpha]_{578}$ −5°, $[\alpha]_{546}$ −5°, $[\alpha]_{436}$ +3°, $[\alpha]_{365}$ +9°, $[\alpha]_{334}$ +25° (*c*=2.0, $CHCl_3$); ir ($CHCl_3$) ν max 1730, 1260–1210 cm^{-1}; *anal.*, calcd for $C_{21}H_{32}O_6$, C 66.29, H 8.48, O 25.23; found C 66.16, H 8.31, O 25.13%.

X-RAY CRYSTALLOGRAPHY.[1]—X-ray data collections were done on a Nicolet R3m four circle diffractometer equipped with CuKα radiation (λ=1.54178 Å). The diffractometer was operated in the θ:2θ scanning mode. Single crystals of **3** and **7** were grown by slow crystallization from $CHCl_3$/hexane. The corresponding crystal data are summarized in Table 4, and their fractional atomic coordinates are given in Table 3. The data measured were corrected for background, Lorentz, and polarization effects, while crystal decay and absorption were negligible. The structures were solved by direct methods using the software provided by the diffractometer manufacturer. For the structural refinements the non-hydrogen atoms were treated anisotropically; the hydroxyl hydrogens of **3** became evident from a ΔF synthesis, and the hydrogen atoms bonded to carbons, included in the structure factor calculation, were refined isotropically. A few reflections were excluded from the final refinement calculations to improve the fit. Molecular models were calculated using the program PCMODEL (4.50), available from Serena Software. The program is a derived version of the MM2 program developed by N.L. Allinger (QCPE 395), University of Georgia.

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