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## Ruthenium-Catalyzed Rearrangement of *ent*-14-(Benzoyloxy)-15,16-epoxybeyerane Diterpenes

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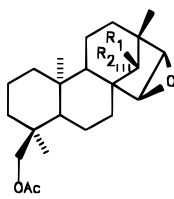
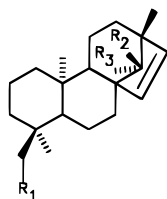
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Rearrangements of *ent*-18-acetoxy-14 $\alpha$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane and *ent*-18-acetoxy-14 $\beta$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane, catalyzed by ruthenium acetylacetonate, were carried out. With the 14-*endo*-(benzoyloxy) compound, *ent*-18-acetoxy-14 $\alpha$ -(benzoyloxy)beyera-9,15-diene, *ent*-18-acetoxy-15 $\alpha$ -(benzoyloxy)-14 $\alpha$ -hydroxykaur-16-ene, *ent*-18-acetoxy-15 $\alpha$ -(benzoyloxy)-14 $\alpha$ -hydroxy-(16*S*)-kaur-11-ene, and *ent*-18-acetoxy-14 $\alpha$ -hydroxy-(16*R*)-kauran-15-one were isolated. However, rearrangement of the 14-*exo*-(benzoyloxy) compound gave *ent*-18-acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxykaur-16-ene, *ent*-18-acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxy-16-ene, *ent*-18-acetoxy-14 $\beta$ -(benzoyloxy)-16 $\beta$ -chloro-15 $\alpha$ -hydroxybeyerane, *ent*-18-acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxy-(16*S*)-kaur-11-ene, *ent*-18-acetoxy-15 $\beta$ -(benzoyloxy)-12 $\alpha$ -chloro-14 $\alpha$ -hydroxy-(16*S*)-kaurane, and *ent*-18-acetoxy-14 $\beta$ -(benzoyloxy)-12 $\alpha$ -chloro-15 $\alpha$ -hydroxybeyerane. The influence of the C-14 benzoyloxy substituent and its arrangement are discussed by comparison with other rearrangement processes reported previously.

### Introduction

Rearrangements of tetracyclic diterpenoids have been extensively studied and were carried out on epoxy compounds<sup>1–9</sup> or thiocarbonates<sup>10</sup> or through solvolytic reactions.<sup>11–18</sup> Recent papers<sup>8,9</sup> have demonstrated that oxygenated functions near the epoxy group participate in the rearrangement process. Moreover, stereochemistry of this function may also influence the course of the reaction.<sup>8,9</sup> In previous papers, ruthenium-catalyzed rearrangements of epoxybeyeranes with 14- or 12-hydroxy and 14- or 12-acetoxy groups were reported.<sup>8,9</sup> In this paper, we investigate the possible participation of a benzoyloxy group in the intermediate structures formed in the rearrangement process and in the yields of products obtained.



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
1	OH	H	OAc
2	OH	H	OH
3	OAc	H	OH
4	OAc	=O	
5	OAc	OH	H

	R <sub>1</sub>	R <sub>2</sub>
6	OBz	H
7	H	OBz

### Results and Discussion

Saponification of *ent*-14 $\beta$ -acetoxy-18-hydroxybeyer-15-ene (**1**), a natural product isolated from *Sideritis pusilla*,<sup>19,20</sup> gave tartesidiol (**2**),<sup>8</sup> which was acetylated to obtain 18-acetoxy derivative **3**.<sup>8</sup> Product **3** was oxidized

with Jones' reagent, yielding ketone **4**, which was reduced with NaBH<sub>4</sub> to give *ent*-18-acetoxy-14 $\alpha$ -hydroxybeyer-15-ene (**5**).<sup>8</sup> Treatment of product **5** with benzoyl chloride gave an *ent*-14 $\alpha$ -(benzoyloxy) derivative, which was epoxidized with *m*-CPBA to obtain *ent*-18-acetoxy-14 $\alpha$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (**6**). Product **3** was treated with benzoyl chloride and afterwards with *m*-CPBA to give *ent*-18-acetoxy-14 $\beta$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (**7**).

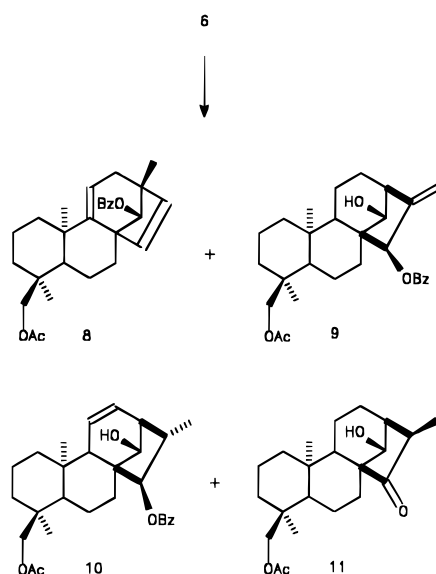
The reaction of *ent*-14 $\beta$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxy derivative **6** with ruthenium acetylacetonate in a sealed tube at 140 °C for 7 h gave rise to a mixture of products **8** (5%), **9** (19%), **10** (8%), and **11** (15%) (Scheme 1). These rearranged products were similar to those obtained previously in which the starting material was the *ent*-14 $\alpha$ -acetoxy-15 $\alpha$ ,16 $\alpha$ -epoxy derivative.<sup>8</sup> Spectroscopic data of products **8–10** were very similar to those of the acetoxy derivatives isolated in previous work, with the expected differences produced by the benzoyloxy group at C-14 or C-15 in the *ent*-beyerene or *ent*-kaurene skeletons, respectively. Formation of these rearranged products from the benzoyloxy epoxy compound **6** has been explained through a process similar to that described for the acetoxy derivatives<sup>8</sup> (Scheme 2). As can be seen, the proposed mechanism assumed different pathways involving hydride shifts and/or the participation of a 14-*endo*-(benzoyloxy) group.

Treatment of epoxy compound **7** with ruthenium acetylacetonate under the above conditions gave **12** (4%), **13** (7%), **14** (10%), **15** (6%), **16** (5%), and **17** (16%) (Scheme 3). In this case, the rearrangement process gave rise to three new rearranged compounds (products **13**, **16**, and **17**). Moreover, other products differed only in the substituent at C-14 and C-15, now a benzoyloxy group instead of an acetoxy group.

Product **12** was similar to a product obtained from an epoxy acetoxy compound<sup>8</sup> and had an *ent*-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxykaur-16-ene skeleton. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data of **12** confirmed this structure, and its formation was justified by the mechanism shown in Scheme 4. An opening of the epoxy group

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**Scheme 1.** Rearrangement of Product **6**

toward C-15 was assumed, and a concerted 12(13)→16 rearrangement could occur. Thus, the *ent*-kaurene skeleton with a carbocation at the original C-13 was formed (path a in Scheme 4). The participation of an *ent*-14 $\beta$ -(benzoyloxy) group gave an intermediate B, which by loss of a C-17 proton yielded product **12** (path b in Scheme 4).

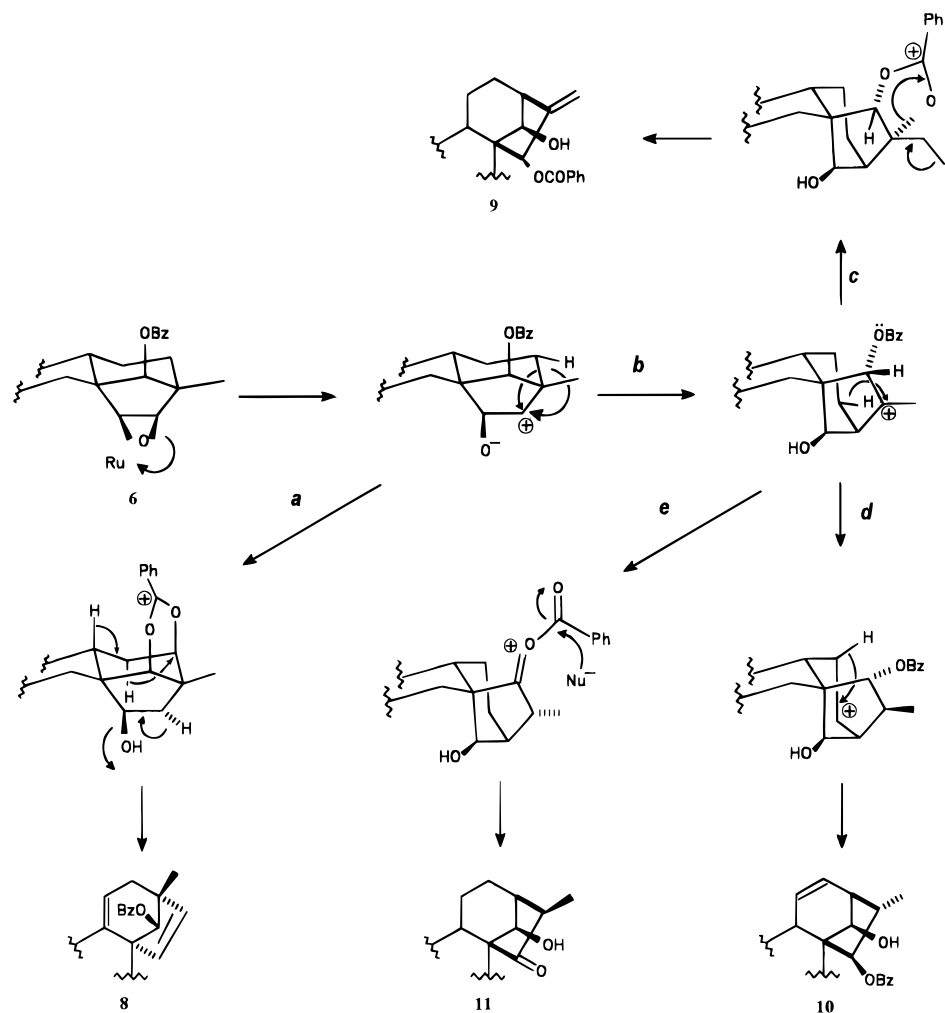
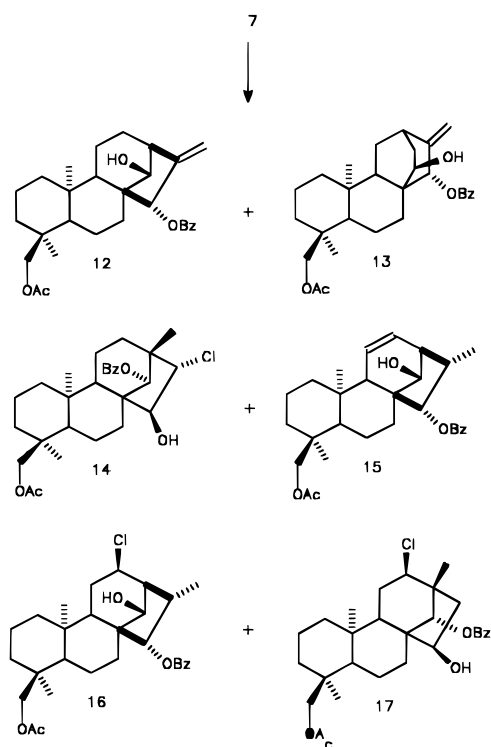
The  $^1\text{H}$  NMR data for rearranged product **13** showed signals similar to those of the previous *ent*-kaurene **12**. Thus, there were *exo*-methylene signals at  $\delta$  4.96 (1H, d,  $J = 2.0$  Hz) and at  $\delta$  5.03 (1H, d,  $J = 2.0$  Hz). The signals for geminal protons to oxygenated functions on C-14 ( $\delta$  4.21, 1H, br d) and C-15 ( $\delta$  5.53, 1H, dd,  $J_1 = 2.0$  Hz,  $J_2 = 4.0$  Hz) can be also observed. The structure of **13** was established using the C/H correlation and COSY experiments. These data suggested the existence of an *ent*-atis-16-ene skeleton functionalized at C-14 and C-15 using published data as a reference for this unfunctionalized skeleton.<sup>21</sup> Thus, the signals at  $\delta$  5.53 (H-15) and  $\delta$  4.21 (H-14) were correlated with the signals at 81.8 ppm (C-15) and 66.7 ppm (C-14) in the correlation C/H spectrum, respectively. Moreover, the H-17 signals were assigned to an *exo*-methylene group at  $\delta$  5.03 and  $\delta$  4.96 in the COSY spectrum. The H-14 signal was coupled to the signal at  $\delta$  2.32 (H-13), which was coupled to another at  $\delta$  2.50 (H-12) in the COSY spectrum. Furthermore, the  $\gamma$ ,  $\beta$ , and  $\alpha$  effects of the C-14 and C-15 substituents on the carbons of the C and D rings were taken into account to assign the chemical shifts in the  $^{13}\text{C}$  NMR spectrum of product **13**. Finally, oxidation of product **13** gave ketone **18**. Several  $^1\text{H}$  and  $^{13}\text{C}$  mono- and bidimensional NMR experiments were conducted on **13**, and these data were in agreement with published data for similar structures.<sup>22</sup> Therefore, product **18** was considered to be the 14-oxo derivative of **13**, which was *ent*-18-acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxyatis-16-ene. The formation of rearranged product **13** was explained according to path c in Scheme 4. Starting from intermediate A, intermediate C was obtained by a 12→16 hydride shift. The participation of an *ent*-14 $\alpha$ -(benzoyloxy) group is possible by the formation of an 1,3-dioxolan-2-ilio cation, and an 16-(13)→12 rearrangement could thus occur (path d in Scheme 4), leading to intermediate D. The process

ended with five-membered ring opening and loss of an H-17 to give the *ent*-atis-16-ene structure **13**.

Product **14**, also obtained from this rearrangement, presented a molecular peak of  $m/z$  502 that indicated a molecular formula of  $\text{C}_{29}\text{H}_{39}\text{O}_5\text{Cl}$ . This product had an *ent*-beyerane skeleton, since its NMR spectrum showed three methyl singlet signals ( $\delta$  1.00, 0.93, and 0.79) and an AB quartet from the C-18 acetoxyethylene group. In addition, the *ent*-14 $\beta$ -(benzoyloxy) group also remained at this position, since the signal of its geminal proton appeared at  $\delta$  4.91 (1H, d,  $J = 1$  Hz). Moreover, the signals of protons geminal to functions on C-15 and C-16 were apparent at  $\delta$  4.41 (1H, m) and  $\delta$  4.14 (1H, d,  $J = 3.9$  Hz), respectively. These signals were similar to those observed for a previously described *ent*-16 $\beta$ -chloro-15 $\alpha$ -hydroxy derivative obtained from *trans* epoxy opening.<sup>9</sup> The  $^{13}\text{C}$  NMR data of **14** were also compatible with the mentioned substitution for similar compounds.<sup>8,9</sup> Product **14** was probably formed from intermediate A by dorsal attack of a chlorine ion on C-16 (path e in Scheme 4). Such chlorine entry was observed previously<sup>9</sup> and probably originated from the solvent ( $\text{CHCl}_3$ ) in which the rearrangement process was conducted.

Rearranged product **15** had an *ent*-kaur-11-ene skeleton and was similar to a product obtained from the acetoxy epoxy compound rearranged previously.<sup>8</sup> Its formation was started from intermediate B by a 12→16 hydride shift (path f in Scheme 4) so that a carbonium ion was formed at C-12 (intermediate E). This cationic structure may undergo the loss of a C-11 proton with the formation of a C-11/C-12 double bond (path g in Scheme 4).

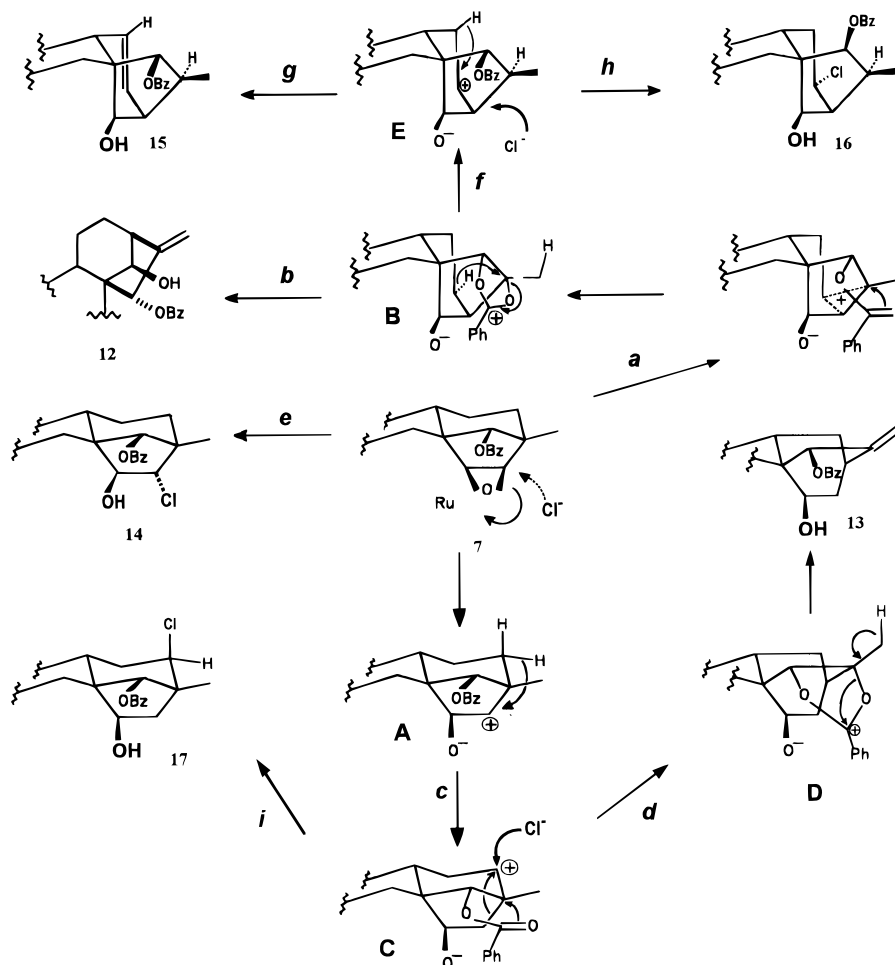
Product **16** also differed from derivatives previously obtained.<sup>8</sup> Its molecular ion peak ( $m/z$  502) and the successive fragmentations observed indicated that a chlorinated compound was again formed, with a molecular formula of  $\text{C}_{29}\text{H}_{39}\text{O}_5\text{Cl}$ . The  $^1\text{H}$  NMR spectrum of **16** presented two singlet methyls ( $\delta$  0.97 and 0.79) and one doublet methyl ( $\delta$  1.10,  $J = 8.0$  Hz); in addition, a double quartet was observed at  $\delta$  2.73 (1H, dq,  $J_1 = J_2 = 8.0$  Hz). These signals suggested that **16** had an *ent*-kaurane structure. Several bidimensional NMR experiments were done to establish the structure of this compound. At  $\delta$  5.22 there was a signal (1H, d,  $J = 8.0$  Hz) which was coupled with the signal at  $\delta$  2.73 (H-16); therefore, the  $\delta$  5.22 signal was due to the proton at C-15 geminal to a benzoyloxy group. Moreover, the signal of the *ent*-14 $\beta$  proton geminal to hydroxyl group (1H, s) was located at  $\delta$  4.14. In addition, at 4.25 ppm we noted the signal of a proton coupled with three other protons (1H, ddd,  $J_1 = 12.0$  Hz,  $J_2 = 6.2$  Hz,  $J_3 = 2.3$  Hz). Since there was a chlorine in the molecule, this signal must represent its geminal proton. From the COSY spectrum of **16** we deduced that the signal at  $\delta$  4.25 (*ent*-12 $\beta$ -H) was correlated with three proton signals at  $\delta$  2.32, 2.13, and 1.65. Therefore, a  $\text{CHCHXCH}_2$  group must be present, an arrangement that is only possible if the chlorine atom is situated at C-11 or C-12. The C/H correlation spectrum of **16** was also studied and the  $^{13}\text{C}$  NMR chemical shifts were analyzed, assuming both possibilities. On the basis of these data and the  $^{13}\text{C}$  NMR chemical shifts for related *ent*-kaurane compounds,<sup>8,23</sup> we conclude that product **16** was *ent*-18-acetoxy-15 $\beta$ -(benzoyloxy)-12 $\alpha$ -chloro-14 $\alpha$ -hy-

**Scheme 2.** Proposed Mechanism of Rearrangement of Epoxy Compound **6****Scheme 3.** Rearrangement of Product **7**

droxykaurane. The formation of **16** could be explained by an attack by chlorine ion on the intermediate E (path

h in Scheme 4) only on the *ent*- $\alpha$  face because of marked steric hinderance on the *ent*- $\beta$  face.

The last product isolated from this rearrangement (**17**) also had a molecular formula of  $C_{29}H_{39}O_5Cl$  ( $m/z$  502). Product **17** had an *ent*-beyerane skeleton, since three methyl singlet signals at  $\delta$  1.12, 1.00, and 0.80 were observed in the  $^1H$  spectrum. At  $\delta$  5.42 we noted a singlet signal corresponding to a proton geminal to the benzoyloxy group on C-14. Moreover, at 4.10 ppm (1H, narrow doublet,  $J = 1.7$  Hz) and 4.35 ppm (1H, broad multiplet) we found the signals of two protons geminal to the hydroxy group and to the chlorine atom. The  $^{13}C$  NMR data were not compatible with products formed from a *trans* or *cis* epoxy group opening. Various 2D-experiments (COSY, C/H, and INADEQUATE) were done to unequivocally establish the structure of compound **17**. An INADEQUATE spectrum study allowed us to determine the connectivity of all carbons of the molecule. An *ent*-beyerane skeleton was assumed for compound **17**, and its INADEQUATE spectrum showed that C-15 was oxygenated and that it was connected to a quarternary (C-8) and a methylenic carbon atom (C-16). Furthermore, C-16 was joined to a primary carbon (C-17), to a methynic carbon (C-12), and to the carbon which supported the benzoyloxy group (C-14). NOE effects were observed between H-17, H-12, and H-14; there was also a NOE effect between H-15 and H-20. Therefore, compound **17** is assumed to have an axial chlorine atom at C-12 and *ent*-15 $\alpha$ -hydroxyl group at

**Scheme 4.** Proposed Mechanism of Rearrangement of Epoxy Compound **7**

C-15. We therefore conclude that **17** had a structure of *ent*-18-acetoxy-14 $\beta$ -(benzoyloxy)-12 $\alpha$ -chloro-15 $\alpha$ -hydroxybeyerane. The formation of compound **17** from **7** could easily be justified via intermediate **C** by an attack by chlorine ion at C-12 (path i in Scheme 4).

The results reported here indicate that rearrangement of the 14-(benzoyloxy) epoxy compounds **6** and **7** instead of the 14-acetoxy epoxy compounds<sup>8</sup> does not lead to a significant improvement in yield. However, in the case of *ent*-14 $\beta$ -(benzoyloxy) derivative **7**, the resulting products varied considerably. The *ent*-atis-16-ene product **13** is interesting because it can be used as a precursor for *ent*-14-oxo atis-16-enes. These *ent*-atisenes possess interesting biological properties and have been isolated from tropical plants.<sup>24</sup> In addition, the chlorinated compounds obtained allowed us to postulate a mechanism of formation of the products by capture of intermediates from the rearrangement process.

## Experimental Section

**General Experimental Procedures.** NMR spectra were done in CDCl<sub>3</sub> in a Bruker AM-300 Bruker and in a ARX-400. The assignments of <sup>13</sup>C chemical shifts were done with the aid of distortionless enhancement by polarization transfer (DEPT) using a flip angle of 135°. 2D-NMR experiments, COSY90, NOESY, direct C/H correlation, and INADEQUATE, were performed with pullprogrs from the Bruker library (COSY90, NOESYST, HXCO, and INAD respectively). A sample

of 110 mg of product **17** in 0.5 mL of CDCl<sub>3</sub> in a 5 mm diameter probe was used for INADEQUATE, which was acquired by 512 experiences of 192 scans, with relaxation delay between scans of 2.2 s and refocalization time of 1/4J = 0.0065 s, in a week-end experiment. IR spectra were recorded on a Perkin-Elmer Model 983 G spectrometer or on a Nicolet 20SX FT-IR spectrometer. Mass spectra were determined with CI (methane) in a Hewlett-Packard Model 5988 A spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 20 °C. Silica gel SDS 60 A CC (40–60  $\mu$ m) was used for flash chromatography. CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> containing increasing amounts of Me<sub>2</sub>CO was used as the eluent. Analytical plates (silica gel, Merck 60 G) were rendered visible by spraying with H<sub>2</sub>SO<sub>4</sub>/AcOH, followed by heating to 120 °C. Starting material for this work, *ent*-14 $\beta$ -acetoxy-18-hydroxybeyer-15-ene (**1**), was isolated from *Sideritis pusilla* (var. flavovirens).<sup>19,20</sup>

**Saponification of *ent*-14 $\beta$ -Acetoxy-18-hydroxybeyer-15-ene (**1**).** Seven hundred mg of **1** was dissolved in 25 mL of a MeOH/H<sub>2</sub>O solution (30/70) with 5% of KOH. The reaction was maintained at reflux for 6 h, after which time it was neutralized, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by flash chromatography, yielding 600 mg of **2** (98%).<sup>8</sup>

**Acetylation of *ent*-14 $\beta$ ,18-Dihydroxybeyer-15-ene (**2**).** Six hundred mg of **2** was acetylated with Ac<sub>2</sub>O/Py (2:4 mL) for 1 h at 0 °C. Purification by flash chromatography provided 110 mg of monoacetylated product **3** (76%).<sup>8</sup>

**Oxidation of *ent*-18-Acetoxy-14 $\beta$ -hydroxybeyer-15-ene (3).** Three hundred mg of **3** was dissolved in acetone (10 mL) and oxidized with Jones' reagent for 30 min at 0 °C. Purification by flash chromatography gave 235 mg of **4** (79%).<sup>8</sup>

**Reduction with NaBH<sub>4</sub> of *ent*-18-Acetoxybeyer-15-en-14-one (4).** Twenty mg of NaBH<sub>4</sub> was added to a stirred solution of 235 mg of **4** in EtOH (10 mL) at room temperature for 1 h. The reaction mixture was acidified with dilute HCl, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried, and evaporated. Purification by flash chromatography provided 228 mg of **5** (96%).<sup>8</sup>

**Benzoylation and Epoxidation of *ent*-18-Acetoxy-14 $\alpha$ -hydroxybeyer-15-ene (5).** Two hundred twenty-eight mg of **5** was treated with benzoyl chloride/Py (1:2 mL). After 12 h at room temperature, the mixture was diluted with H<sub>2</sub>O, extracted with CHCl<sub>3</sub>, washed with saturated KHSO<sub>4</sub>, dried, and evaporated. Purification by flash chromatography gave *ent*-18-acetoxy-14 $\alpha$ -(benzoyloxy)beyer-15-ene. This benzoyloxy derivative was epoxidized with 200 mg of *m*-CPBA in 5 mL of CHCl<sub>3</sub> for 24 h at room temperature. The reaction mixture was then diluted with CHCl<sub>3</sub>, washed with aqueous FeSO<sub>4</sub>, aqueous NaHCO<sub>3</sub>, and water, dried, and concentrated. Purification by flash chromatography provided *ent*-18-acetoxy-14 $\alpha$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (**6**) (148 mg, 65%).

***ent*-18-Acetoxy-14 $\alpha$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (6):** mp 45–47 °C; [ $\alpha$ ]<sub>D</sub><sup>20</sup> –41° (c 0.5, CHCl<sub>3</sub>); IR  $\nu$ (max) (CHCl<sub>3</sub>) 1725, 1270, 1248; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 8.09–7.45 (5H, PhCOO), 4.66 (1H, s, H-14), 3.81 (1H, Q<sub>AB</sub>, *J* = 10.9 Hz, H-18), 3.63 (1H, d, *J* = 3.5 Hz, H-15), 3.60 (1H, Q<sub>AB</sub>, *J* = 10.9 Hz, H-18), 3.22 (1H, d, *J* = 3.5 Hz, H-16), 1.84 (3H, s, MeCOO), 1.04, 1.01, 0.85 (3H each, s); <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>) 39.3 (C-1), 18.3 (C-2), 35.8 (C-3), 36.5 (C-4), 48.3 (C-5), 19.3 (C-6), 30.1 (C-7), 45.5 (C-8), 50.0 (C-9), 37.2 (C-10), 17.8 (C-11), 29.2 (C-12), 40.8 (C-13), 78.0 (C-14), 55.1 (C-15), 59.0 (C-16), 19.4 (C-17), 73.0 (C-18), 17.6 (C-19), 16.2 (C-20), 20.8 (MeCO), 171.2 (MeCO), 166.2 (PhCOO), 133.2, 130.5, 129.6, 128.6 (PhCOO); CIMS (CH<sub>4</sub>) *m/z* 467 [M + 1]<sup>+</sup> (16), 407 (58), 345 (100), 285 (77). Anal. Calcd for C<sub>29</sub>H<sub>38</sub>O<sub>5</sub>: C, 74.68; H, 8.15. Found: C, 74.5; H, 8.3.

**Benzoylation and Epoxidation of *ent*-18-Acetoxy-14 $\beta$ -hydroxybeyer-15-ene (3).** The procedure was the same as that described for the preparation of epoxy benzoyloxy derivative **6**. Thus, product **3** (200 mg) was converted into *ent*-18-acetoxy-14 $\beta$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (**7**) (210 mg, 78%).

***ent*-18-Acetoxy-14 $\beta$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (7):** mp 63–65 °C; [ $\alpha$ ]<sub>D</sub><sup>20</sup> + 22° (c 0.5, CHCl<sub>3</sub>); IR  $\nu$ (max) 1728, 1265, 1245; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 8.11–7.39 (5H, PhCOO), 4.65 (1H, s, H-14), 3.79 (1H, Q<sub>AB</sub>, *J* = 11.0 Hz, H-18), 3.61 (1H, dd, *J*<sub>1</sub> = 2.9 Hz, *J*<sub>2</sub> = 1.1 Hz, H-15), 3.61 (1H, Q<sub>AB</sub>, *J* = 11.0 Hz, H-18), 3.19 (1H, dd, *J*<sub>1</sub> = 2.9 Hz, *J*<sub>2</sub> = 1.3 Hz, H-16), 2.03 (3H, s, MeCOO), 1.04, 0.99, 0.83 (3H each, s); <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>) 39.0 (C-1), 17.8 (C-2), 35.6 (C-3), 36.4 (C-4), 49.3 (C-5), 18.8 (C-6), 27.8 (C-7), 49.1 (C-8), 56.6 (C-9), 37.6 (C-10), 17.8 (C-11), 34.8 (C-12), 44.6 (C-13), 85.2 (C-14), 55.3 (C-15), 59.6 (C-16), 17.7 (C-17), 72.7 (C-18), 16.9 (C-19), 16.1 (C-20), 21.1 (MeCO), 171.3 (MeCO), 167.2 (PhCOO), 132.9, 130.3, 129.9, 128.4 (PhCOO); CIMS (CH<sub>4</sub>) *m/z* 467 [M + 1]<sup>+</sup> (22), 345 (100), 285 (68). Anal.

Calcd for C<sub>29</sub>H<sub>38</sub>O<sub>5</sub>: C, 74.68; H, 8.15. Found: C, 74.8; H, 8.2.

**Rearrangement of *ent*-18-Acetoxy-14 $\alpha$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (6).** Product **6** (140 mg) was dissolved in CHCl<sub>3</sub> (5 mL) in a sealed tube. Then, 14 mg of ruthenium acetylacetonate was added, and the mixture was heated at 140 °C for 7 h. The solution was concentrated, and after purification and separation by flash chromatography four products were obtained: **8** (7 mg, 5%), **9** (27 mg, 19%), **10** (11 mg, 8%), and **11** (8), (16 mg, 15%).

***ent*-18-Acetoxy-14 $\alpha$ -(benzoyloxy)beyer-9,15-diene (8):** mp syrup; [ $\alpha$ ]<sub>D</sub><sup>20</sup> + 35° (c 0.5, CHCl<sub>3</sub>); IR  $\nu$ -(max) 1724, 1675, 1266; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 8.06–7.42 (5H, PhCOO), 6.20 (1H, d, *J* = 6.1 Hz, H-15), 5.40 (1H, dd, *J*<sub>1</sub> = *J*<sub>2</sub> = 3.5 Hz, H-11), 5.36 (1H, d, *J* = 6.1 Hz, H-16), 4.91 (1H, s, H-14), 3.82 (1H, Q<sub>AB</sub>, *J* = 11.0 Hz, H-18), 3.49 (1H, Q<sub>AB</sub>, *J* = 11.0 Hz, H-18), 2.22 (1H, Q<sub>AB</sub>, *J* = 2.9 Hz, H-12), 2.16 (1H, Q<sub>AB</sub>, *J* = 2.9 Hz, H-12), 1.55 (3H, s, MeCOO), 1.11, 1.02, 0.83 (3H each, s); <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>) 37.8 (C-1), 18.3 (C-2), 35.7 (C-3), 36.8 (C-4), 44.9 (C-5), 19.3 (C-6), 33.1 (C-7), 49.2 (C-8), 152.1 (C-9), 38.7 (C-10), 116.0 (C-11), 31.6 (C-12), 43.1 (C-13), 83.1 (C-14), 142.1 (C-15), 132.4 (C-16), 22.3 (C-17), 72.2 (C-18), 17.9 (C-19), 25.3 (C-20), 20.3 (MeCO), 171.2 (MeCO), 166.8 (PhCOO), 133.0, 130.7, 129.7, 128.5 (PhCOO); CIMS (CH<sub>4</sub>) *m/z* 449 [M + 1]<sup>+</sup> (6), 329 (100), 327 (10), 269 (23), 267 (8). Anal. Calcd for C<sub>29</sub>H<sub>36</sub>O<sub>4</sub>: C, 77.68; H, 8.04. Found: C, 77.5; H, 7.9.

***ent*-18-Acetoxy-15 $\alpha$ -(benzoyloxy)-14 $\alpha$ -hydroxykaur-16-ene (9):** mp 68–70 °C; [ $\alpha$ ]<sub>D</sub><sup>20</sup> –74° (c 0.5, CHCl<sub>3</sub>); IR  $\nu$ (max) 3421, 1729, 1267, 1229; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 8.11–7.46 (5H, PhCOO), 5.78 (1H, dd, *J*<sub>1</sub> = *J*<sub>2</sub> = 2.5 Hz, H-15), 5.13 (1H, br s, H-17), 5.11 (1H, d, *J* = 2.5 Hz, H-17), 4.34 (1H, s, H-14), 3.78 (1H, Q<sub>AB</sub>, *J* = 10.9 Hz, H-18), 3.64 (1H, Q<sub>AB</sub>, *J* = 10.9 Hz, H-18), 2.74 (1H, br s, H-13), 1.94 (3H, s, MeCOO), 1.06, 0.82 (3H each, s); <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>) 40.3 (C-1), 18.1 (C-2), 35.7 (C-3), 36.6 (C-4), 50.8 (C-5), 19.5 (C-6), 29.9 (C-7), 51.7 (C-8), 50.4 (C-9), 39.2 (C-10), 17.8 (C-11), 33.7 (C-12), 49.6 (C-13), 75.2 (C-14), 79.9 (C-15), 151.8 (C-16), 110.0 (C-17), 73.4 (C-18), 18.5 (C-19), 17.5 (C-20), 19.3 (MeCO), 171.4 (MeCO), 166.8 (PhCOO), 133.2, 130.7, 129.9, 128.7 (PhCOO); CIMS (CH<sub>4</sub>) *m/z* 467 [M + 1]<sup>+</sup> (1), 449 (26), 345 (16), 327 (18), 285 (100), 267 (15). Anal. Calcd for C<sub>29</sub>H<sub>38</sub>O<sub>5</sub>: C, 74.68; H, 8.15. Found: C, 74.8; H, 8.0.

***ent*-18-Acetoxy-15 $\alpha$ -(benzoyloxy)-14 $\alpha$ -hydroxy-16(S)-kaur-11-ene (10):** mp 138–40 °C; [ $\alpha$ ]<sub>D</sub><sup>20</sup> –133° (c 0.5, CHCl<sub>3</sub>); IR  $\nu$ (max) 3515, 1716, 1274, 1237; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 8.05–7.42 (5H, PhCOO), 6.09 (1H, ddd, *J*<sub>1</sub> = 9.7 Hz, *J*<sub>2</sub> = 7.0 Hz, *J*<sub>3</sub> = 1.7 Hz, H-12), 5.48 (1H, dd, *J*<sub>1</sub> = 9.7 Hz, *J*<sub>2</sub> = 3.6 Hz, H-11), 4.99 (1H, d, *J* = 3.6 Hz, H-15), 4.47 (1H, br s, H-14), 3.82 (1H, Q<sub>AB</sub>, *J* = 10.9 Hz, H-18), 3.64 (1H, Q<sub>AB</sub>, *J* = 10.9 Hz, H-18), 2.47 (1H, dd, *J*<sub>1</sub> = 3.9 Hz, *J*<sub>2</sub> = 1.7 Hz, H-16), 2.29 (1H, dd, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 2.4 Hz, H-13), 2.12 (1H, d, *J* = 7.1 Hz, H-9), 1.93 (3H, s, MeCOO), 1.35 (d, *J* = 7.4 Hz, 3H-17), 0.98, 0.82 (3H each, s); <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>) 39.8 (C-1), 17.8 (C-2), 35.6 (C-3), 36.5 (C-4), 49.0 (C-5), 19.8 (C-6), 28.0 (C-7), 52.1 (C-8), 49.4 (C-9), 38.4 (C-10), 134.0 (C-11), 125.2 (C-12), 54.3 (C-13), 75.7 (C-14), 90.8 (C-15), 48.3 (C-16), 20.7 (C-17), 73.1 (C-18), 17.7 (C-19), 17.5 (C-20), 21.3 (MeCO), 171.3 (MeCO), 166.7 (PhCOO), 132.9, 131.0, 129.6, 128.5 (PhCOO); CIMS (CH<sub>4</sub>) *m/z* 467 [M + 1]<sup>+</sup> (6), 345 (56), 327 (35), 285 (100), 267 (28). Anal.

Calcd for  $C_{29}H_{38}O_5$ : C, 74.68; H, 8.15. Found: C, 74.8, H, 8.0.

**Rearrangement of ent-18-Acetoxy-14 $\beta$ -(benzoyloxy)-15 $\alpha$ ,16 $\alpha$ -epoxybeyerane (7).** Product **7** (837 mg) was dissolved in  $CHCl_3$  (15 mL) in a sealed tube. Then, 80 mg of ruthenium acetylacetonate was added, and the mixture was heated at 140 °C for 7 h. The solution was concentrated, and after purification and separation by flash chromatography six products were obtained: **12** (33 mg, 4%), **13** (58 mg, 7%), **14** (85 mg, 9.5%), **15** (50 mg, 6%), **16** (45 mg, 5%), and **17** (143 mg, 16%).

**ent-18-Acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxykaur-16-ene (12):** mp 127–29 °C;  $[\alpha]_D^{20} +5^\circ$  (*c* 0.5,  $CHCl_3$ ); IR  $\nu$ (max) 3424, 1712, 1273;  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ ) 8.00–7.40 (5H, PhCOO), 5.62 (1H, s, H-15), 5.37 (1H, s, H-17), 5.28 (1H, s, H-17), 4.22 (1H, br s, H-14), 3.78 (1H,  $Q_{AB}$ ,  $J = 10.9$  Hz, H-18), 3.62 (1H,  $Q_{AB}$ ,  $J = 10.9$  Hz, H-18), 2.02 (3H, s, MeCOO), 1.05, 0.81 (3H each, s);  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ) 39.8 (C-1), 17.9 (C-2), 35.6 (C-3), 36.5 (C-4), 49.8 (C-5), 18.8 (C-6), 27.1 (C-7), 53.2 (C-8), 56.7 (C-9), 39.6 (C-10), 18.4 (C-11), 33.1 (C-12), 51.4 (C-13), 76.7 (C-14), 82.7 (C-15), 152.7 (C-16), 114.8 (C-17), 72.8 (C-18), 17.9 (C-19), 17.5 (C-20), 21.2 (MeCO), 171.4 (MeCO), 166.4 (PhCOO), 133.2, 130.2, 129.8, 128.6 (PhCOO); CIMS ( $CH_4$ )  $m/z$  467  $[M + 1]^+$  (1), 449 (7), 345 (14), 327 (15), 285 (100), 267 (16). Anal. Calcd for  $C_{29}H_{38}O_5$ : C, 74.68; H, 8.15. Found: C, 74.8; H, 8.1.

**ent-18-Acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxyatis-16-ene (13):** mp 58–60 °C;  $[\alpha]_D^{20} +45^\circ$  (*c* 1,  $CHCl_3$ );  $\nu$ (max) 3420, 1718, 1269;  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ ) 8.00–7.40 (5H, PhCOO), 5.53 (1H, dd,  $J_1 = 2.0$  Hz,  $J_2 = 4.0$  Hz, H-15), 5.03 (1H, d,  $J = 2.0$  Hz, H-17), 4.96 (1H, d,  $J = 2.0$  Hz, H-17), 4.21 (1H, br d, H-14), 3.81 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 3.63 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 2.50 (1H, m, H-12), 2.05 (3H, s, MeCOO), 0.96, 0.82 (3H each, s);  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ) 39.0 (C-1), 17.7 (C-2), 35.7 (C-3), 36.4 (C-4), 49.8 (C-5), 17.4 (C-6), 29.9 (C-7), 41.8 (C-8), 50.6 (C-9), 37.7 (C-10), 27.0 (C-11), 35.6 (C-12), 40.4 (C-13), 66.7 (C-14), 81.8 (C-15), 149.9 (C-16), 110.9 (C-17), 72.6 (C-18), 17.6 (C-19), 15.1 (C-20), 21.2 (MeCO), 171.4 (MeCO), 166.6 (PhCOO), 133.4, 130.0, 129.6, 128.8 (PhCOO); CIMS ( $CH_4$ )  $m/z$  467  $[M + 1]^+$  (29), 449 (4), 345 (81), 327 (26), 285 (52). Anal. Calcd for  $C_{29}H_{38}O_5$ : C, 74.68; H, 8.15. Found: C, 74.4; H, 8.3.

**ent-18-Acetoxy-14 $\beta$ -(benzoyloxy)-15 $\alpha$ -hydroxy-16 $\beta$ -chlorobeyerane (14):** mp 115–17 °C;  $[\alpha]_D^{20} +17.2^\circ$  (*c* 0.5,  $CHCl_3$ ); IR  $\nu$ (max) 3497, 1718, 1272;  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ ) 8.00–7.40 (5H, PhCOO), 4.91 (1H, d,  $J = 1.7$  Hz, H-14), 4.41 (1H, m, H-15), 4.14 (1H, d,  $J = 3.9$  Hz, H-16), 3.74 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 3.60 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 2.03 (3H, s, MeCOO), 1.00, 0.93, 0.79 (3H each, s);  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ) 39.0 (C-1), 17.5 (C-2), 35.4 (C-3), 36.3 (C-4), 49.5 (C-5), 18.5 (C-6), 27.7 (C-7), 49.4 (C-8), 55.7 (C-9), 37.9 (C-10), 19.0 (C-11), 33.1 (C-12), 47.0 (C-13), 91.2 (C-14), 80.5 (C-15), 77.0 (C-16), 19.4 (C-17), 72.8 (C-18), 17.8 (C-19), 15.2 (C-20), 21.1 (MeCO), 171.3 (MeCO), 166.0 (PhCOO), 133.3, 129.7, 129.7, 128.6 (PhCOO); CIMS ( $CH_4$ )  $m/z$  503  $[M + 1]^+$  (2), 487 (3), 485 (7), 383 (3), 381 (9), 365 (23), 363 (65), 323 (33), 321 (100), 305 (37), 303 (98). Anal. Calcd for  $C_{29}H_{38}O_5Cl$ : C, 69.32; H, 7.57. Found: C, 69.2; H, 7.7.

**ent-18-Acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxy-16(S)-kaur-11-ene (15):** mp 135–37 °C;  $[\alpha]_D^{20} -12.5^\circ$  (*c* 1,  $CHCl_3$ ); IR  $\nu$ (max) 3502, 3012, 1715, 1279;  $^1H$  NMR

( $\delta$ ,  $CDCl_3$ ) 8.10–7.40 (5H, PhCOO), 6.02 (1H, ddd,  $J_1 = 9.7$  Hz,  $J_2 = 7.1$  Hz,  $J_3 = 1.6$  Hz, H-12), 5.33 (1H, dd,  $J_1 = 9.7$  Hz,  $J_2 = 3.6$  Hz, H-11), 5.21 (1H, d,  $J = 8.0$  Hz, H-15), 4.35 (1H, s, H-14), 3.78 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 3.65 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 2.69 (1H, dq,  $J_1 = J_2 = 8.0$  Hz, H-16), 2.02 (3H, s, MeCOO), 1.07 (d,  $J = 8.0$  Hz, 3H-17), 0.96, 0.81 (3H each, s);  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ) 39.3 (C-1), 17.8 (C-2), 35.5 (C-3), 36.5 (C-4), 49.7 (C-5), 19.1 (C-6), 27.0 (C-7), 52.0 (C-8), 62.3 (C-9), 38.8 (C-10), 134.4 (C-11), 124.2 (C-12), 49.0 (C-13), 74.6 (C-14), 86.0 (C-15), 46.8 (C-16), 16.7 (C-17), 72.9 (C-18), 17.7 (C-19), 17.6 (C-20), 21.2 (MeCO), 171.5 (MeCO), 166.3 (PhCOO), 133.0, 130.4, 129.7, 128.6 (PhCOO); CIMS ( $CH_4$ )  $m/z$  467  $[M + 1]^+$  (1), 345 (15), 285 (100), 267 (56). Anal. Calcd for  $C_{29}H_{38}O_5$ : C, 74.68; H, 8.15. Found: C, 74.9; H, 7.9.

**ent-18-Acetoxy-15 $\beta$ -(benzoyloxy)-12 $\alpha$ -chloro-14 $\alpha$ -hydroxykaurane (16):** mp 156–58 °C;  $[\alpha]_D^{20} +11.0^\circ$  (*c* 0.5,  $CHCl_3$ ); IR  $\nu$ (max) 3508, 1714, 1279;  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ ) 8.03–7.40 (5H, PhCOO), 5.22 (1H, d,  $J = 8.0$  Hz, H-15), 4.25 (1H, ddd,  $J_1 = 12.0$  Hz,  $J_2 = 6.2$  Hz,  $J_3 = 2.3$  Hz, H-12), 4.14 (1H, s, H-14), 3.77 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 3.60 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 2.01 (3H, s, MeCOO), 1.10 (d,  $J = 8.0$  Hz, 3H-17), 0.97, 0.79 (3H each, s);  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ) 39.8 (C-1), 17.9 (C-2), 35.4 (C-3), 36.4 (C-4), 49.4 (C-5), 18.9 (C-6), 27.1 (C-7), 53.1 (C-8), 58.4 (C-9), 39.2 (C-10), 30.1 (C-11), 60.8 (C-12), 56.0 (C-13), 76.8 (C-14), 84.4 (C-15), 35.0 (C-16), 17.2 (C-17), 72.6 (C-18), 18.4 (C-19), 17.5 (C-20), 21.1 (MeCO), 171.3 (MeCO), 166.0 (PhCOO), 133.2, 129.7, 128.6, 128.5, (PhCOO); CIMS ( $CH_4$ )  $m/z$  503  $[M + 1]^+$  (1), 487 (2), 485 (5), 468 (4), 365 (4), 363 (10), 323 (33), 321 (100), 305 (12), 303 (33). Anal. Calcd for  $C_{29}H_{38}O_5Cl$ : C, 69.32; H, 7.57. Found: C, 69.2; H, 7.7.

**ent-18-Acetoxy-14 $\beta$ -(benzoyloxy)-12 $\alpha$ -chloro-15 $\alpha$ -hydroxybeyerane (17):** mp 129–31 °C;  $[\alpha]_D^{20} +3.8^\circ$  (*c* 1,  $CHCl_3$ ); IR  $\nu$ (max) 3526, 1718, 1275;  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ ) 8.00–7.40 (5H, PhCOO), 5.42 (1H, s, H-14), 4.35 (1H, m, H-15), 4.10 (1H, d,  $J = 1.7$  Hz, H-12), 3.78 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 3.61 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 2.07 (3H, s, MeCOO), 1.12, 1.00, 0.80 (3H each, s);  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ) 38.9 (C-1), 17.5 (C-2), 35.3 (C-3), 36.4 (C-4), 49.4 (C-5), 18.7 (C-6), 27.5 (C-7), 52.4 (C-8), 49.6 (C-9), 37.4 (C-10), 28.8 (C-11), 68.2 (C-12), 48.5 (C-13), 88.0 (C-14), 72.1 (C-15), 49.4 (C-16), 20.2 (C-17), 72.5 (C-18), 17.8 (C-19), 16.1 (C-20), 21.2 (MeCO), 171.4 (MeCO), 165.8 (PhCOO), 133.3, 129.9, 129.6, 128.7 (PhCOO); CIMS ( $CH_4$ )  $m/z$  503  $[M + 1]^+$  (6), 487 (4), 485 (11), 383 (3), 381 (9), 365 (6), 363 (18), 323 (33), 321 (100). Anal. Calcd for  $C_{29}H_{38}O_5Cl$ : C, 69.32; H, 7.57. Found: C, 69.1; H, 7.6.

**Oxidation of ent-18-Acetoxy-15 $\beta$ -(benzoyloxy)-14 $\alpha$ -hydroxyatis-16-ene (13).** Product **13** (50 mg) was oxidized with Jones' reagent for 6 h as described above, and after flash chromatography ent-18-acetoxy-15 $\beta$ -(benzoyloxy)atis-16-en-14-one (**18**) was obtained (40 mg, 86%).

**ent-18-Acetoxy-15 $\beta$ -(benzoyloxy)atis-16-en-14-one (18):** mp 66–68 °C;  $[\alpha]_D^{20} -64.0^\circ$  (*c* 0.5,  $CHCl_3$ ); IR  $\nu$ (max) 2950, 1733, 1240;  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ ) 7.95–7.38 (5H, PhCOO), 5.62 (1H, s, H-14), 5.19 (1H, s, H-17), 5.15 (1H, s, H-17), 3.80 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 3.60 (1H,  $Q_{AB}$ ,  $J = 11.0$  Hz, H-18), 2.84 (1H, m, H-12), 2.04 (3H, s, MeCOO), 0.80, 0.77 (3H each, s);  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ) 38.4 (C-1), 17.4 (C-2), 35.7 (C-3), 36.3 (C-4),

48.9 (C-5), 18.6 (C-6), 28.0 (C-7), 51.8 (C-8), 48.9 (C-9), 38.0 (C-10), 28.6 (C-11), 37.2 (C-12), 44.2 (C-13), 213.2 (C-14), 79.1 (C-15), 147.8 (C-16), 114.0 (C-17), 72.6 (C-18), 17.8 (C-19), 14.2 (C-20), 21.2 (MeCO), 171.3 (MeCO), 166.3 (PhCOO), 133.3, 129.9, 129.8, 128.5 (PhCOO); CIMS (CH<sub>4</sub>) *m/z* 465 [M + 1]<sup>+</sup> (5), 343 (100), 283 (80). Anal. Calcd for C<sub>29</sub>H<sub>36</sub>O<sub>5</sub>: C, 75.00; H, 7.76. Found: C, 74.8; H, 8.0.

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