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Lathyrane Diterpenoids from the Roots of *Euphorbia micractina* and Their Biological Activities

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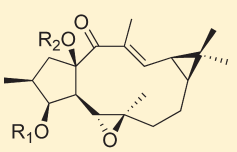
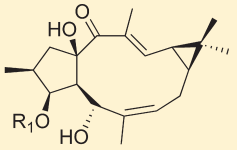
Supporting Information

ABSTRACT: Seventeen new lathyrane diterpenoids (**1**−**17**) and two known analogues have been isolated from an ethanolic extract of *Euphorbia micractina* roots. Their structures including absolute configurations were determined by spectroscopic data interpretation and single-crystal X-ray crystallography. Compound **10** showed activity against HIV-1 replication in vitro, with an IC_{50} value of 8.2 μM. Compounds **6**, **7**, **11**, **14**, **15**, and **18**, at 10^{-6} M, showed significant vascular-relaxing activities against phenylephrine-induced vasoconstriction with relaxation rates of 48%, 41%, 42%, 48%, 50%, and 53%, respectively.



1 R_1 = R_2 = Ac



12 R_1 = cinnamoyl

Lathyrane diterpenoids with a 5/11/3-membered ring system are common in *Euphorbia* species.[1] Recently, considerable attention has been devoted to lathyrane derivatives as apoptosis inducers and multidrug resistance modulators in cancer cells.[2−7] Continuing our investigation of the Chinese folk medicine *Euphorbia micractina* Boiss (Euphorbiaceae),[8−12] with focus on minor diterpenoids from an EtOH extract of roots of this plant, 17 new (**1**−**17**) and two known lathyrane diterpenoids have been isolated. This paper describes the isolation, structure elucidation, and in vitro bioassays of the new isolates.

RESULTS AND DISCUSSION

Compound **1**, molecular formula $C_{24}H_{34}O_6$ by HRESIMS, was obtained as colorless crystals. The presence of ester carbonyl and conjugated ketone groups (1738, 1659, and 1631 cm^{-1}) was evident in its IR spectrum. The NMR spectra of **1** showed resonances characteristic for 3,15-dioxy-5,6-epoxylathyr-12-en-14-one derivatives,[4,13−16] consisting of 5 × CH_3, 3 × CH_2, 7 × CH (two oxygen-bearing and an olefinic), and 5 × C (two oxygen-bearing, a carbonyl, and an olefinic) (Tables 1 and 3), and additional resonances for two acetyl groups. This combined with the chemical shifts of H-3, C-3, and C-15 indicated that **1** was 3,15-diacetoxy-5,6-epoxylathyr-12-en-14-one. The suggestion was supported by 2D NMR data analysis of **1** (Supporting Information, Figures S8−S10) that amended the assignments of the 1D NMR data (Tables 1 and 3). In order to determine the absolute configuration of **1**, a single-crystal X-ray crystallographic analysis using anomalous scattering of Cu Kα radiation was carried out. An ORTEP drawing, with the atom numbering indicated, is shown in Figure 1. This indicated that the configuration of the 5,6-epoxy ring in derivatives of jolkinol had been incorrectly proposed.[14,17] Therefore, compound **1** was determined to be (−)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-3,15-diacetoxy-5,6-epoxylathyr-12-en-14-one.

Compound **2** had the molecular formula $C_{22}H_{32}O_5$ (by HRESIMS) and showed UV and IR data similar to those of **1**. Comparison of the NMR data between **2** and **1** (Tables 1 and 3) indicated that one OAc in **1** was replaced by an OH in **2**. In addition, C-12 and C-14 in **2** were deshielded by $\Delta\delta_C$ +3.2 and +4.2 ppm, respectively, whereas C-15 was shielded by $\Delta\delta_C$ −3.8 ppm. This suggested that compound **2** was the 15-deacetyl derivative of **1**, which was verified by 2D NMR data (Supporting Information, Figures S20−S22). The similarity of coupling constants (Table 1), NOE enhancements, and Cotton effects between **2** and **1** (Supporting Information, Figures S4, S11−S13 and S16, S23−S25) revealed that the two compounds had the same configuration. This was confirmed by alkaline hydrolysis of both **2** and **1** that yielded the same product, (−)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-5,6-epoxylathyr-12-ene-3,15-diol-14-one[13] (Experimental Section). Thus, compound **2** was elucidated as (−)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-3-acetoxy-5,6-epoxylathyr-12-en-15-ol-14-one.

Compound **3** was the 3-deacetyl analogue of **1**, as indicated by its spectroscopic data (Tables 1 and 3 and Experimental Section). The NMR data indicated that C-2 and C-4 in **3** were deshielded by $\Delta\delta_C$ +1.2 and +1.9 ppm, respectively, whereas H-3 and C-3 were shielded by $\Delta\delta_H$ −1.33 and $\Delta\delta_C$ −1.7 ppm, indicating replacement of the 3-OAc in **1** by a 3-OH in **3**. This was confirmed by $^1H-^1H$ gCOSY data (Supporting Information, Figure S32) and alkaline hydrolysis of **3** that gave the same hydrolysate as that from **1** (Experimental Section). Therefore, compound **3** was assigned as (−)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,-11*S*,15*R*)-15-acetoxy-5,6-epoxylathyr-12-en-3-ol-14-one, which was previously reported as the epoxidation product of jolkinol D in the literature, but without supporting spectroscopic data.[13]

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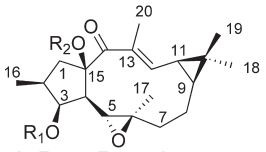
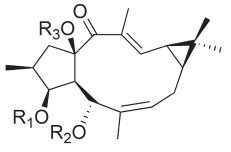
Table 1. ^{1}H NMR Data (δ) for the Diterpene Moiety of Compounds 1−8 in Me_2CO-d_6[a,b]

no.	1	2	3	4	5	6	7	8
1a	3.38 dd (13.2, 7.8)	3.14 dd (12.6, 7.2)	3.30 dd (13.2, 7.8)	3.20 dd (13.0,7.5)	3.67 dd (14.0, 7.5)	3.23 dd (12.5, 7.0)	3.55 d (13.0, 8.0)	3.51 dd (14.5, 8.5)
1b	1.50 t (13.2)	1.62 t (12.6)	1.61 t (13.2)	1.69 t (13.0)	1.85 m	1.80 t (12.5)	1.66 t (13.0)	1.47 m
2	2.02 m	1.89 m	1.80 m	1.99 m	2.28 m	2.05 m	2.15 m	2.16 m
3	5.29 t (3.6)	5.25 t (3.6)	3.96 dt (5.4, 3.6)	5.42 t (4.0)	5.71 t (3.5)	5.54 t (4.0)	5.42 t (4.0)	5.24 br s
4	1.65 dd (9.0, 3.6)	1.58 (9.0, 3.6)	1.40 dd (9.6, 3.6)	1.64 (9.5, 4.0)	1.49 (9.0, 3.5)	1.75 dd (9.0, 4.0)	1.82 dd (9.0, 4.0)	2.50 dd (11.0, 3.5)
5	3.34 d (9.0)	3.32 d (9.0)	3.48 d (9.6)	3.37 d (9.5)	3.68 d (9.0)	3.42 d (9.0)	3.62 d (9.0)	5.35 d (11.0)
7a	2.02 m	1.98 m	2.04 m	1.95 m	1.95 m	1.94 m	2.00 m	2.50 m
7b	1.42 m	1.38 m	1.45 m	1.36 m	1.39 m	1.30 m	1.46 m	1.76 dt (12.5, 1.5)
8a	2.00 m	1.96 m	2.04 m	1.95 m	1.98 m	1.94 m	1.90 m	2.20 m
8b	1.58 m	1.61 m	1.62 m	1.59 m	1.40 m	1.58 m	1.46 m	1.55 m
9	1.22 m	1.20 m	1.24 m	1.20 m	1.16 m	1.19 m	1.17 m	1.06 m
11	1.58 dd (10.8, 8.4)	1.63 dd (11.4, 8.4)	1.62 dd (12.0, 8.4)	1.64 dd (11.5, 7.5)	1.57 dd (11.0, 7.5)	1.64 dd (11.5, 8.0)	1.55 dd (11.5, 8.0)	1.40 dd (11.0, 8.0)
12	6.97 dd (10.8, 0.6)	7.82 dd (11.4, 1.2)	7.01 dd (12.0, 1.2)	7.85 d (11.5)	7.08 d (11.0)	7.87 d (11.5)	7.02 d (11.5)	6.67 d (11.0)
16	0.89 d (6.6)	0.90 d (6.6)	1.02 d (6.0)	0.94 d (7.0)	0.97 d (6.5)	0.94 d (7.0)	0.94 d (7.0)	0.95 d (6.5)
17	1.12 s	1.16 s	1.12 s	1.19 s	1.19 s	1.19 s	1.15 s	1.45 s
18	1.19 s	1.19 s	1.20 s	1.22 s	1.04 s	1.19 s	1.04 s	1.17 s
19	1.08 s	1.06 s	1.11 s	1.07 s	0.31 s	1.07 s	0.28 s	1.05 s
20	1.79 d (0.6)	1.80 d (1.2)	1.79 d (1.2)	1.82 s	1.86 s	1.84 s	1.83 s	1.84 s
OH-3/15		/4.91 s	3.80 d (5.4)/	/4.93 s		/5.19 s		

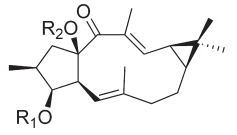
[a] Data (δ) were measured in acetone-d_6 for **1**−**3** at 600 MHz and for **4**−**7** at 500 MHz and in $CDCl_3$ for **8** at 500 MHz. Coupling constants (J) in Hz are given in parentheses. The assignments were based on DEPT, ^{1}H−^{1}H COSY, HSQC, and HMBC experiments. [b] Data for acyl units: see Experimental Section.



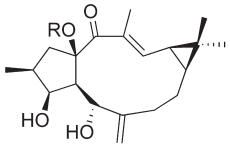
1 R_1 = R_2 = Ac
2 R_1 = Ac, R_2 = H
3 R_1 = H, R_2 = Ac
4 R_1 = cinnamoyl, R_2 = H
5 R_1 = R_2 = benzoyl
6 R_1 = benzoyl, R_2 = H
7 R_1 = Ac, R_2 = benzoyl



12 R_1 = cinnamoyl, R_2 = R_3 = H
13 R_1 = R_3 = H, R_2 = cinnamoyl
14 R_1 = Ac, R_2 = H, R_3 = benzoyl
15 R_1 = H, R_2 = Ac, R_3 = benzoyl
16 R_1, R_2 = isopropylidene, R_3 = cinnamoyl
18 R_1 = R_2 = H, R_3 = benzoyl



8 R_1 = R_2 = Ac
9 R_1 = cinnamoyl, R_2 = H
10 R_1 = H, R_2 = cinnamoyl
11 R_1 = H, R_2 = benzoyl



17 R = cinnamoyl

Compound **4**, molecular formula $C_{29}H_{36}O_5$ by HRESIMS, showed NMR data similar to those of **2** except for substitution of the resonances for OAc in **2** by those attributable to a cinnamoyl group in **4** (Tables 1 and 3 and Experimental Section). 2D NMR, NOE, and CD data (Supporting Information, Figure S35−S43) combined with alkaline hydrolysis (Experimental Section) of **4** proved that it was (+)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-3-cinnamoyloxy-5,6-epoxylathyr-12-en-15-ol-14-one.

Compound **5** had the molecular formula $C_{34}H_{38}O_6$, as indicated by HRESIMS. The NMR data of **5** (Tables 1 and 3 and Experimental Section) demonstrated that it was another analogue of **1** where the acetyl groups were substituted by benzoyl groups. This was confirmed also by gHMBC data (Supporting Information, Figure S49) and alkaline hydrolysis (Experimental Section) of **5**. Thus, compound **5** was assigned to be (−)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-3,15-dibenzoyloxy-5,6-epoxylathyr-12-en-14-one.

Compound **6**, molecular formula $C_{27}H_{34}O_5$ by HRESIMS, displayed UV and IR data (Tables 1 and 3 and Experimental Section) similar to those of **5**. Comparison of the NMR data between **6** and **5** demonstrated the presence of an OH [δ_H 5.19 (s)] in **6** replacing a benzoyloxy group in **5**. In addition, H-12 and H_3-19 and C-12 and C-14 in **6** were deshielded by $\Delta\delta_H$ +0.79 and +0.76 and $\Delta\delta_C$ +2.3 and +4.6 ppm, respectively, whereas C-15 was shielded by $\Delta\delta_C$ −4.9 ppm. This revealed that **6** was the 15-debenzoyl analogue of **5**. In the HMBC spectrum (Supporting Information, Figure S58), correlations from O*H* to C-4, C-14, and C-15 verified the location of OH at C-15 in **6**. Accordingly, compound **6** was determined to be (+)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-3-benzoyloxy-5,6-epoxylathyr-12-en-15-ol-14-one.

The spectroscopic data of compound **7** (Tables 1 and 2 and Experimental Section) indicated that it was an analogue of **1** with the molecular formula $C_{29}H_{36}O_6$. Comparison of the NMR data of **7** and **1** indicated substitution of one OAc in **1** by a benzoyloxy group in **7**. In addition, H_3-19 in **7** was significantly shielded by $\Delta\delta_H$ −0.80. This revealed that the benzoyloxy group was located at C-15 in **7** since similar shielding effects were observed only in lathyrane derivatives with a benzoyloxy group at C-15.[9,14,16] Thus, compound **7** was determined to be (−)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-3-acetoxy-15-benzoyloxy-5,6-epoxylathyr-12-en-14-one.

Compound **8** had the molecular formula $C_{24}H_{34}O_5$, one less oxygen atom than **1**. The main difference in the NMR data between **8** and **1** was replacement of the resonances for the sp^3 hybrid H-5, C-5, and C-6 of the trisubstituted epoxy ring in **1** by those due to a sp^2 hybrid trisubstituted double bond unit in **8** (Tables 1 and 3 and Experimental Section). This revealed that **8** was the deoxy-5-ene analogue of **1**, which was proved by 2D NMR data (Supporting Information, Figures S72−S74). In the NOE difference spectrum of **8**, irradiation of H-5 gave enhancement of H_2-7, demonstrating the *E*-configuration for the double bond between C-5 and C-6. Epoxidation of **8** with *m*-chloroperbenzoic acid in CH_2Cl_2 yielded **1**.[13] Hence, compound **8** was elucidated as (−)-(5*E*,12*E*,2*S*,3*S*,4*S*,9*S*,11*S*,15*R*)-3,15-diacetoxylathyra-5,12-dien-14-one.

Compound **9**, molecular formula $C_{29}H_{36}O_4$, had NMR spectra (Tables 2 and 3) similar to those of **8**. The two OAc resonances

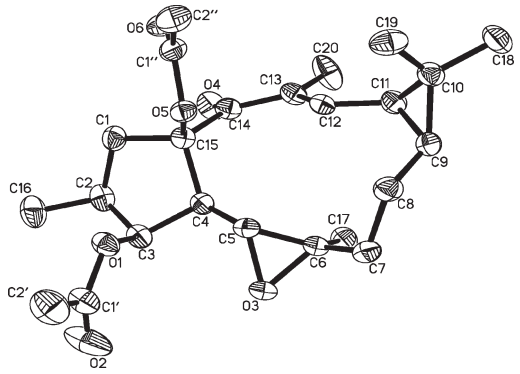


Figure 1. ORTEP diagram of compound **1**.

in **8** were replaced by those of cinannamoyloxy and OH groups in **9**. In addition, C-15 in **9** was shielded by $\Delta\delta_C$ −3.6 ppm when compared to that of **8**, whereas C-12 and C-14 were deshielded by $\Delta\delta_C$ +3.4 and +3.9 ppm, respectively. The difference between **8** and **9** was similar to that between **4** and **1**, indicating that the cinnamoyloxy and OH groups were located at C-3 and C-15 in **9**, respectively. In the HMBC spectrum of **9** (Supporting Information, Figure S86), correlations for O*H*/C-4, C-14, and C-15 confirmed the OH at C-15. The configuration of **9** was demonstrated by the NOE difference experiment (Supporting Information, Figures S87−S90), and alkaline hydrolysis of **8** and **9** yielded the same diterpene diol (Experimental Section). Therefore, compound **9** was determined to be (+)-(5*E*,12*E*,2*S*,-3*S*,4*S*, 9*S*,11*S*,15*R*)-3-cinnamoyloxylathyra-5,12-dien-14-one.

Comparison of the NMR spectra of compounds **10** and **9** (Tables 2 and 3) indicated that they differed by replacement of the exchangeable singlet for O*H*-15 in **9** with an exchangeable doublet due to O*H*-3 in **10**. Meanwhile, H-3 and C-3 in **10** were shielded by $\Delta\delta_H$ −1.44 and $\Delta\delta_C$ −2.8 ppm, respectively, whereas C-15 was deshielded by $\Delta\delta$ +4.7 ppm. This indicated that **10** was the 15-cinnamoyloxy isomer of **9**, which was supported by HRESIMS and confirmed by alkaline hydrolysis of **10** producing the same diterpene diol as that from **9** (Experimental Section). Hence, compound **10** was defined to be (−)-(5*E*,12*E*,2*S*,3*S*,4*S*,9*S*,-11*S*,15*R*)-15-cinnamoyloxylathyra-5,12-dien-3-ol-14-one.

The spectroscopic data of compound **11** (Tables 2 and 3 and Experimental Section) demonstrated that it was an analogue of **10** where the cinnamoyl was substituted by a benzoyl group. This was shown by characteristic benzoyl resonances in the NMR spectra of **11** that replaced those of the cinnamoyl group in **10**. The location of the benzoyloxy at C-15 in **11** was demonstrated by shifts for H-3 and H_3-19 and C-3, C-12, C-14, and C-15 (Tables 2 and 3).[9,14,16] Therefore, compound **11** was assigned to be (−)-(5*E*,12*E*,2*S*,3*S*,4*S*,9*S*,11*S*,15*R*)-15-benzoyloxylathyra-5,12-dien-3-ol-14-one, which was confirmed by alkaline hydrolysis (Experimental Section) and 2D NMR data (Supporting Information, Figures S102−S104).

Compound **12** had the molecular formula $C_{29}H_{36}O_5$, as indicated by HRESIMS. Comparison of the NMR data of **12** and **9** (Tables 2 and 3 and Experimental Section) demonstrated that resonances attributable to an oxymethine in **12** [δ_H 5.07 (1H, d, J = 9.0 Hz, H-5) and δ_C 64.1] replaced those of one aliphatic methylene (CH_2-7) in **9**. The shifts and coupling constants for resonances of one trisubstituted double bond in **12** were significantly different from those of the double bond between C-5 and C-6 in **9**. This suggested that **12** was a 5-hydroxy-6-ene or 7-hydroxy-5-ene derivative of **9**. In the HMBC spectrum (Supporting Information, Figure S115), correlations from H-5 to C-4, C-7, C-15, and C-17, from H_3-17 to C-5, C-6, and C-7, from H_3-20 to C-12, C-13, and C-14, from both H-3 and O*H*-15 to C-15, and from H-3 to C-1′, in combination with shifts of these proton and carbon resonances, demonstrated that **12** was the 5-hydroxy-6-ene derivative of **9**. In the NOE difference spectrum of **12**, irradiation of H-12 enhanced H-5, H-8a, and H_3-19, while irradiation of H_3-19 gave enhancements of H-8a and H-12. In addition, H-9, H_3-18, and H_3-20 were enhanced upon irradiation of H-11, and irradiation of H_3-17 enhanced H-4 and H-7. The enhancements, together with the similarity of the CD data between **12** and **9** (Supporting Information, Figures S110 and S80), demonstrated that **12** had the 6*Z*,12*E*,2*S*,3*S*,4*R*,5*R*,9*S*,11*S*,15*R* configuration. Thus, compound **12** was elucidated as (−)-(6*Z*,12*E*,2*S*,3*S*,4*R*,-5*R*,9*S*,11*S*,15*R*)-3-cinnamoyloxylathyra-6,12-diene-5,15-diol-14-one.

Compound **13** was the 5-cinnamoyloxy isomer of **12**, as indicated by the spectroscopic data (Tables 2 and 3 and Experimental Section) and confirmed by its 2D NMR and CD data and enhancements of H-8a, H-12, and O*H*-15 upon irradiation of H-5 in the NOE difference experiment of **13** (Supporting Information, Figures S121 and S125−S129). Thus, compound **13** was assigned to be (−)-(6*Z*,12*E*,2*S*,3*S*,4*R*,5*R*,9*S*,11*S*,15*R*)-5-cinnamoyloxylathyra-6,12-diene-3,15-diol-14-one.

Compound **14** was an analogue of **12** having the molecular formula $C_{29}H_{36}O_6$. Comparison of the NMR data of **14** and **12** revealed signals of OAc and benzoyloxy groups in **14**, instead of the cinnamoyloxy and OH in **12**. The shifts of H-3, H-5, and H_3-19 and C-3, C-5, C-12, C-14, and C-15 in **14** (Tables 2 and 3) indicated that the OAc and benzoyloxy groups were at C-3 and C-15 in **14**, respectively.[9,14,16] The suggestion was proved by 2D NMR, NOE, and CD data of **14** (Supporting Information, Figures S132−S142). Thus, compound **14** was determined to be (−)-(6*Z*,12*E*,2*S*,3*S*,4*R*,5*R*,9*S*,11*S*,15*R*)-3-acetoxy-15-benzoyloxylathyra-6,12-dien-5-ol-14-one.

Compound **15** was the 5-acetoxy isomer of **14**, as indicated by the spectroscopic data (Tables 2 and 3 and Experimental Section) and confirmed by the 2D NMR and CD data (Supporting Information, Figures S145−S152). Alkaline hydrolysis of **12**−**15** yielded the same diterpene triol (Experimental Section). Hence, compound **15** was assigned to be (−)-(6*Z*,12*E*,2*S*,3*S*,-4*R*,5*R*,9*S*,11*S*,15*R*)-5-acetoxy-15-benzoyloxylathyra-6,12-dien-3-ol-14-one.

Comparison of the NMR data of compounds **16** and **13** (Tables 2 and 3 and Experimental Section) indicated that the resonances for O*H*-3 and O*H*-15 in **13** were replaced by those assignable to an isopropylidene unit in **16**. In addition, H-3, H-4, H-5, and H-12 as well as C-1, C-3, C-4, C-5, C-7, C-12, C-14, and C-16 in **16** were shielded, whereas H-1a and C-6, C-9, C-10, C-13, and C-15 were deshielded. Meanwhile, the coupling constant between H-4 and H-5 was changed from 10.5 Hz in **13** to 5.5 Hz in **16**. In the NOE difference spectrum of **16**, irradiation of H-3 gave enhancements of H-4 and the proton resonance for one methyl group of the isopropylidene unit, while irradiation of H-5 enhanced H-8a, H-12, and the proton resonance for the other methyl group of the isopropylidene unit. The data suggested that compound **16** was the 3,5-acetonide-15-cinnamoyloxy derivative of **13**, which was supported by HRESIMS (molecular formula $C_{32}H_{40}O_5$) and confirmed by 2D NMR data (Supporting Information, Figures S158−S160). Therefore, compound **16** was (−)-(6*Z*,12*E*,2*S*,-3*S*,4*R*,5*R*,9*S*,11*S*,15*R*)-15-cinnamoyloxy-3,5-di-*O*-isopropylidenelathyra-6,12-dien-14-one. This compound was considered to be a natural product since acetonation of the triol obtained by

Table 2. ^{1}H NMR Data (δ) for the Diterpene Moiety of Compounds 9−17 in Me_2CO-d_6[a,b]

no.	9	10	11	12	13	14	15	16	17
1a	3.29 dd (13.2, 7.8)	3.40 dd (13.5, 8.0)	3.46 dd (13.0, 7.5)	3.17 dd (14.0, 10.0)	3.15 dd (13.0, 11.0)	3.39 dd (15.0, 9.6)	3.32 dd (14.0, 8.5)	3.33 dd (13.0, 7.0)	3.33 dd (13.2, 7.2)
1b	1.57 t (13.2)	1.59 t (13.5)	1.65 t (13.0)	1.61 dd (14.0, 9.5)	1.56 m	1.77 dd (15.0, 9.6)	1.80 dd (14.0,11.5)	1.62 t (13.0)	1.76 t (13.2)
2	2.08 m	1.95 m	1.98 m	2.29 m	2.00 m	2.32 m	2.06 m	2.02 m	2.00 m
3	5.35 t (4.2)	3.91 m	3.98 m	5.80 t (4.0)	4.46 br s	5.78 t (4.2)	4.39 dt (6.5, 3.0)	4.02 t (4.0)	4.34 dt (6.6, 3.6)
4	2.47 dd (10.8, 4.2)	2.40 dd (11.0, 3.5)	2.47 dd (11.0, 3.5)	2.33 dd (9.0, 4.0)	2.40 dd (10.5, 2.5)	2.53 dd (9.0, 4.2)	2.41 dd (8.5, 3.0)	2.12 m	2.44 dd (8.4, 3.6)
5	5.52 dd (10.8, 1.8)	5.92 d (11.0)	6.02 d (11.0)	5.07 d (9.0)	6.39 d (10.5)	5.24 m	6.76 d (8.5)	5.41 d (5.5)	4.94 t (8.4)
7a	2.40 dt (13.2,3.0)	2.55 dt (13.0, 3.0)	2.56 m	5.03 dd (12.0, 1.5)	5.17 d (10.5)	5.09 dd (12.6, 2.4)	5.20 dd (12.5, 3.0)	5.27 dd (12.0, 3.0)	2.73 dd (13.2, 4.2)
7b	1.74 td (13.2, 2.4)	1.81 dt (13.0, 2.5)	1.82 m						2.14 dt (13.2, 2.4)
8a	2.08 m	2.17 m	2.15 m	2.38 m	2.71 m	2.26 m	2.56 m	2.45 m	1.94 m
8b	1.49 m	1.59 m	1.40 m	2.15 m	2.25 m	2.13 m	2.14 m	2.29 m	1.69 m
9	1.08 m	1.08 m	1.02 m	1.20 m	1.23 m	1.17 m	1.19 m	1.34 m	1.14 m
11	1.49 dd (12.0 7.8)	1.44 dd (11.5, 8.5)	1.38 m	1.51 m	1.56 m	1.38 dd (12.0, 9.0)	1.39 dd (11.5, 9.0)	1.43 (11.0, 8.5)	1.38 dd (10.8, 8.4)
12	7.48 dd (12.0,1.2)	6.78 d (11.5)	6.69 d (11.5)	7.87 d (11.5)	7.97 d (11.5)	6.59 dd (12.0, 1.2)	6.69 d (11.5)	6.56 d (11.0)	6.49 dd (10.8, 1.2)
16	0.97 d (6.6)	1.05 d (6.5)	1.05 d (7.0)	0.98 d (6.5)	1.08 d (7.0)	0.88 d (6.6)	1.00 d (7.0)	1.01 d (7.0)	1.05 d (6.6)
17	1.52 d (1.8)	1.49 s	1.50 s	1.51 s	1.51 s	1.54 s	1.61 s	1.71 s	4.89 s; 4.72 s
18	1.16 s	1.08 s	1.01 s	1.15 s	1.18 s	0.95 s	0.96 s	1.09 s	1.06 s
19	1.02 s	0.83 s	0.25 s	1.26 s	1.31 s	0.43 s	0.44 s	1.04 s	0.88 s
20	1.80 d (1.2)	1.78 s	1.78 s	1.67 s	1.68 s	1.70 s	1.70 s	1.70 s	1.63 s
O*H*-3/5		3.60 d (5.0)/		/3.50 s	4.46 s/	/3.78 d (4.2)	3.49 d (5.5)/		3.91 d (3.6)/ 4.24 d (8.4)
O*H*-15	4.33 s			4.19 s	4.95 s				

[a] Data (δ) were measured in acetone-d_6 for **9**, **14**, and **17** at 600 MHz and for **10**−**13**, **15**, and **16** at 500 MHz. Coupling constants (J) in Hz are given in parentheses. The assignments were based on DEPT, ^{1}H−^{1}H COSY, HSQC, and HMBC experiments. [b] Data for acyl units: see Experimental Section.

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Table 3. ^{13}C NMR Data (δ) for the Diterpene Moiety of Compounds 1−17[a,b]

no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	45.9	46.8	45.7	47.0	46.8	46.9	46.4	44.7	46.3	44.7	44.6	51.4	50.2	48.4	48.0	47.5	48.0
2	38.2	38.4	39.4	38.7	39.1	38.8	38.8	38.3	38.9	40.3	40.3	37.6	37.6	36.7	39.0	37.4	38.5
3	80.2	81.1	78.5	81.4	81.7	82.0	80.8	81.0	82.3	79.5	79.4	82.3	79.5	80.9	78.9	76.6	79.4
4	51.2	51.1	53.1	51.4	52.5	51.3	52.2	51.2	52.1	54.0	54.1	57.3	55.5	55.8	55.2	53.7	55.3
5	57.5	58.3	58.5	58.3	58.0	58.3	58.0	118.6	121.1	122.2	122.2	64.1	68.1	64.1	66.8	64.1	66.9
6	63.4	63.1	63.4	63.2	63.9	63.2	63.7	143.0	141.6	141.8	142.0	136.9	131.5	136.7	133.0	135.3	149.8
7	39.0	39.6	39.6	39.6	39.3	39.6	39.4	36.8	37.6	37.5	37.6	125.3	128.6	125.7	128.7	126.8	36.1
8	23.6	23.7	23.9	23.8	23.9	23.7	23.9	28.3	29.0	29.0	29.0	24.1	24.2	23.9	24.7	24.5	22.6
9	34.2	34.7	34.4	34.8	34.8	34.7	34.7	34.1	34.7	34.7	34.7	31.5	30.6	31.6	32.0	33.5	35.2
10	26.5	26.5	26.5	26.5	26.8	26.5	26.7	24.5	24.8	24.9	24.8	25.1	24.5	25.3	25.6	27.0	25.2
11	30.6	30.4	30.4	30.5	30.4	30.5	30.3	29.6	29.9	30.2	30.2	28.5	28.3	28.1	28.3	28.0	28.9
12	144.5	147.7	144.3	147.8	145.3	147.6	145.2	146.5	149.9	146.8	146.7	150.0	149.8	144.4	144.2	144.1	146.3
13	134.4	133.8	134.7	133.9	134.6	133.9	134.6	132.2	131.9	132.3	132.4	134.7	130.7	134.1	134.1	132.1	133.5
14	194.8	199.0	195.5	198.9	194.6	199.2	194.7	195.2	199.1	195.6	195.5	201.5	199.8	197.5	197.8	197.5	197.3
15	91.7	87.9	92.6	88.1	92.7	87.8	92.6	94.5	90.9	95.6	95.9	90.6	91.5	94.3	93.9	92.1	93.1
16	13.7	14.1	13.7	14.2	14.1	14.2	13.9	13.8	14.5	14.1	14.0	15.3	15.1	15.1	14.1	13.2	13.8
17	20.0	20.4	20.3	20.4	20.3	20.4	20.3	20.8	20.8	20.8	20.9	18.5	18.8	18.6	18.9	18.4	112.7
18	29.0	29.1	29.1	29.1	29.0	29.1	29.0	29.1	29.2	29.2	29.2	28.6	28.3	28.5	28.5	28.8	29.0
19	16.5	16.4	16.7	16.5	15.4	16.5	15.3	16.3	16.4	16.6	15.3	16.6	16.2	15.8	15.8	17.6	17.0
20	12.4	12.7	12.6	12.7	12.6	12.7	12.6	12.2	12.7	12.5	12.6	12.2	11.9	12.0	12.2	11.9	13.8

[a] Data (δ) were measured in acetone-d_6 for **1**−**3**, **9**, **14**, and **17** at 150 MHz and for **4**−**7**, **11**−**13**, **15**, and **16** at 125 MHz and in $CDCl_3$ for **8** at 125 MHz.. The assignments were based on DEPT, ^{1}H−^{1}H COSY, HSQC, and HMBC experiments. [b] Data for acyl units: see Experimental Section.

alkaline hydrolysis of **13** did not occur when it was refluxed with or without silica gel (the absorbent used in the isolation procedure) in acetone for 48 h.

The spectroscopic data of **17** (Tables 2 and 3 and Experimental Section) indicated that it was an isomer of **12**. Comparison of the NMR data of **17** and **12** revealed an exocyclic terminal double bond between C-6 and C-17 in **17**, replacing the double bond between C-6 and C-7 in **12**. In addition, H-3 and C-3 in **17** were shielded by $\Delta\delta_H$ −1.46 and $\Delta\delta_C$ −2.9 ppm, respectively, whereas C-6 and C-15 were deshielded by $\Delta\delta_C$ +12.9 and +2.5 ppm. This suggested that **17** was the 15-cinnamoyloxy-6(17)-ene isomer of **12**, which was verified by 2D NMR, NOE difference, and CD data of **17** (Supporting Information, Figures S163−S172). Thus, **17** was (+)-(12*E*,2*S*,3*S*,4*R*,5*R*,9*S*,11*S*,15*R*)-15-cinnamoyloxy-lathyra-6(17),12-diene-3,5-diol-14-one, which was reported as the deoxygenated product of jolkinol B treated with neutral alumina at 60 °C without any solvent. However, detailed spectroscopic data were absent in the literature.[13]

The known compounds were identified by comparison of spectroscopic data with those reported in the literature as 15β-*O*-benzoyl-5α-hydroxyisolathyrol (**18**)[9] and jolkinol A.[13,15]

Compound **10** showed in vitro activity against HIV-1 replication (IC_{50} 8.2 μM), and the positive control zidovudine (AZT) gave IC_{50} 0.05 μM. The other compounds were all inactive at concentrations of 10 μM. Compounds **6**, **7**, **11**, **14**, **15**, and **18**, at 10^{-6} M, showed significant vascular-relaxing activities against phenylephrine (PE)-induced vasoconstriction with relaxation rates of 48%, 41%, 42%, 48%, 50%, and 53%, respectively, the positive control (verapamile) exhibited a 44% relaxation at the same concentration, and relaxation rates of the other compounds were lower than 30%. This indicated that a 15-benzoyloxy group may play an important role in the vascular-relaxing activity. Compounds **1**−**17** were also assessed for cytotoxicity against several human cancer cell lines,[18] antioxidant activity against Fe^{2+}-cystine-induced rat liver microsomal lipid peroxidation,[19] and protein tyrosine phosphatase 1B (PTP1B);[20] however, all were inactive at a concentration of 10^{-6} M.

EXPERIMENTAL SECTION

General Experimental Procedures. Optical rotations were measured on a PE model 343 polarimeter. UV spectra were measured on a Cary 300 spectrometer. CD spectra were recorded on a Jasco-815 CD spectrometer. IR spectra were recorded on a Nicolet 5700 FT-IR microscope instrument (FT-IR microscope transmission). 1D and 2D NMR spectra were obtained at 500 or 600 MHz for ^{1}H and 125 or 150 MHz for ^{13}C, respectively, on INOVA 500 MHz, Bruker AV-500, or SYS 600 MHz spectrometers, in acetone-d_6 or $CDCl_3$, with solvent peaks used as references. ESIMS data were measured with a Q-Trap LC/MS/MS (Turbo Ionspray Source) spectrometer. HRESIMS were obtained using an AccuToFCS JMS-T100CS spectrometer. Column chromatography (CC) was performed with silica gel (200−300 mesh, Qingdao Marine Chemical Inc. Qingdao, P. R. China) and Sephadex LH-20 (Amersham Biosciences Inc.). Preparative TLC was preformed using silica gel preparative TLC plates ($HSGF_{254}$, glass precoated, Yantai Jiangyou Silica Gel Development Co. Ltd., Yantai, P. R. China). HPLC separations was performed using a Waters 600 controller, a Waters 600 pump, and a Waters 2487 dual λ absorbance detector, with a Prevail (250 × 10 mm i.d.) column packed with C_{18} (5 μm). TLC was carried out on silica gel GF_{254} plates. Spots were visualized under UV light or by spraying with 5% H_2SO_4 in 95% EtOH followed by heating. Unless otherwise noted, all chemicals were obtained from commercially available sources and were used without further purification.

Plant Material. See ref 5.

Extraction and Isolation. For extraction and preliminary fractionation of the extract, see ref 5. Fraction A3 (4.2 g) was separated by silica gel CC, eluting with a step gradient from 4% to 50% acetone in petroleum ether, to give five subfractions (A3-1−A3-5). A3-3 (303 mg) and A3-4 (206 mg) were chromatographed separately over Sephadex LH-20,

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eluting with petroleum ether−$CHCl_3$−MeOH (5:5:1), and further by normal-phase silica gel CC, eluting with 3% acetone in petroleum ether, to give **8** (100.3 mg) and **9** (2.0 mg), respectively. Fraction A4 (6.5 g) was separated by CC over Sephadex LH-20 eluting with petroleum ether−$CHCl_3$−MeOH (5:5:1) to give A4-1−A4-3, of which A4-2 was further fractioned via silica gel CC eluting with 4% acetone in petroleum ether, to afford A4-2-1−A4-2-5. The mixture A4-2-3 was separated by RP-HPLC, using MeOH−H_2O (80:20), to give **5** (15.0 mg), **11** (6.0 mg), and **16** (2.0 mg). Fraction A9 (6.4 g) was fractionated by silica gel CC, eluting with a gradient of increasing acetone (5−100%) in petroleum ether, to give subfractions A9-1−A9-10. A9-4 (2.7 g) and A9-5 (3.2 g) were separately subjected to flash chromatography over RP silica gel eluting with a gradient of increasing EtOH (0−95%) in H_2O, to afford A9-4-1−A9-4-6 from A9-4 and A9-5-1−A9-5-8 from A9-5. Fractions A9-4-3 (229 mg) and A9-5-4 (500 mg) were separately chromatographed over Sephadex LH-20, eluting with petroleum ether−$CHCl_3$−MeOH (5:5:1), and then purified repeatedly by RP-HPLC, using MeOH−H_2O (80:20), to yield **7** (6.8 mg), **13** (1.1 mg), **14** (2.5 mg), and **15** (2.2 mg) from A9-4-3 and **4** (20.0 mg), **6** (2.6 mg), **10** (5.5 mg), and **12** (4.3 mg) from A9-5-4. Sephadex LH-20 CC of A9-5-3 (340 mg) using petroleum ether−$CHCl_3$−MeOH (5:5:1) afforded **1** (150.6 mg). Fractions A10 (3.9 g), A12 (3.7), and A13 (5.5 g) were separated by silica gel CC, eluting with a gradient of increasing acetone (5−50%) in petroleum ether, to give A10-1−A10-9 from A10, A12-1−A12-8 from A12, and A13-1−A13-8 from A13. Fractionation of A10-6, A12-3, and A13-5 respectively by flash column over RP silica gel eluting with a gradient of increasing EtOH (0−95%) in H_2O afforded A10-6-1−A10-6-5 from A10-6, A12-3-1−A12-3-6 from A12-3, and A13-5-1−A13-5-8 from A13-5. Fractions A10-6-3 (200 mg), A12-3-3 (230 mg), A13-5-5 (400 mg) were chromatographed over Sephadex LH-20, eluting with ether−$CHCl_3$−MeOH (5:5:1), and then by RP semipreparative HPLC, using MeOH−H_2O (80:20), to obtain **2** (5.6 mg) from A10-6-3, **3** (2.7 mg) from A12-3-3, and **17** (1.8 mg) from A13-5-5.

*(−)-(12E,2S,3S,4R,5R,6R,9S,11S,15R)-3,15-Diacetoxy-5,6-epoxylathyr-12-en-14-one (**1**):* colorless crystals (acetone), mp 176−178 °C; $[\alpha]^{20}_D$ −54.9 (*c* 0.21, MeOH); UV (MeOH) λ_{max} (log ε) 209 (4.29), 268 (5.20) nm; CD (MeOH) 220 ($\Delta\varepsilon$ −6.61), 264 ($\Delta\varepsilon$ +3.08), 314 ($\Delta\varepsilon$ −1.44); IR ν_{max} 2980, 2924, 2885, 2865, 1738, 1659, 1631, 1450, 1379, 1363, 1247, 1228, 1149, 1061, 1031, 1011, 962, 933, 862, 804, 776, 625 cm^{-1}; ^1H NMR (acetone-d_6, 600 MHz) data for the diterpene moiety, see Table 1, for the acyl unit δ 2.07 (3H, s, H_3-2′), 2.06 (3H, s, H_3-2″); ^{13}C NMR (acetone-d_6, 150 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 170.1 (C-1′), 20.7 (C-2′), 169.8 (C-1″), 21.3 (C-2″); (+)-ESIMS *m*/*z* 419 $[M + H]^+$, 441 $[M + Na]^+$, 457 $[M + K]^+$; HRESIMS *m*/*z* 441.2274 $[M + Na]^+$ (calcd for $C_{24}H_{34}O_6Na$, 441.2253).

*X-ray Crystallography of Compound **1**.* $C_{24}H_{34}O_6$, *M* = 418.51, orthorhombic, $P2_12_12_1$ (no. 24), *a* = 10.1962(2) Å, *b* = 12.6572(3) Å, *c* = 18.0256(4) Å, $\alpha = \beta = \gamma = 90°$, *V* = 2326.3(9) $Å^3$, *Z* = 4, D_{calcd} = 1.195 g cm^{-3}, 2976 reflections independent, 2963 reflections observed ($|F|^2 \geq 2\sigma|F|^2$), R_1 = 0.0352, wR_2 = 0.1010, *S* = 1.082.

The data were collected on a MACDIP-2030K diffractometer with Cu Kα radiation by using the ω-scan technique to a maximum 2θ value of 114.0°. The crystal structure was solved by direct methods by using SHELXS-97, and all non-hydrogen atoms were refined anisotropically using the least-squares method. All hydrogen atoms were positioned by geometrical calculations and difference Fourier overlapping calculation. The absolute configuration was determined on the basis of the Flack parameter, 0.1(2). Crystallographic data for the structure of **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 809199. Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

*(−)-(12E,2S,3S,4R,5R,6R,9S,11S,15R)-3-Acetoxy-5,6-epoxylathyr-12-en-15-ol-14-one (**2**):* colorless needles (MeOH), mp 186−188 °C; $[\alpha]^{20}_D$ −12.2 (*c* 0.59, MeOH); UV (MeOH) λ_{max} (log ε) 200 (2.07), 269 (2.66) nm; CD (MeOH) 216 ($\Delta\varepsilon$ +1.96), 278 ($\Delta\varepsilon$ +2.80), 317 ($\Delta\varepsilon$ −0.37), 350 ($\Delta\varepsilon$ +0.53) nm; IR ν_{max} 3450, 3051, 2955, 2919, 2852, 1740, 1720, 1650, 1622, 1452, 1408, 1379, 1237, 1209, 1148, 1053, 1019, 998, 937, 906, 858, 808, 781, 606, 564 cm^{-1}; ^1H NMR (acetone-d_6, 600 MHz) data for the diterpene moiety, see Table 1, for the acyl unit δ 2.08 (3H, s, H_3-2′); ^{13}C NMR (acetone-d_6, 150 MHz) data for the diterpene moiety, see Table 3, the acyl unit δ 170.3 (C-1′), 20.8 (C-2′); (+)-ESIMS *m*/*z* 377 $[M + H]^+$, 399 $[M + Na]^+$, 415 $[M + K]^+$; (+)-HRESIMS *m*/*z* 415.1933 $[M + K]^+$ (calcd for $C_{22}H_{32}O_5K$, 415.1887).

*(−)-(12E,2S,3S,4R,5R,6R,9S,11S,15R)-15-Acetoxy-5,6-epoxylathyr-12-en-3-ol-14-one (**3**):* white, amorphous powder; $[\alpha]^{20}_D$ −41.4 (*c* 0.15, MeOH); UV (MeOH) λ_{max} (log ε) 208 (4.45), 268 (5.03) nm; CD (MeOH) 221 ($\Delta\varepsilon$ −4.60), 266 ($\Delta\varepsilon$ +6.19) nm; IR ν_{max} 3319, 2962, 2927, 2871, 1747, 1629, 1453, 1415, 1372, 1265, 1235, 1157, 1064, 1037, 1010, 918, 904, 886, 814, 790, 729, 689, 644, 597, 578 cm^{-1}; ^1H NMR (acetone-d_6, 600 MHz) data for the diterpene moiety, see Table 1, for the acyl unit δ 2.03 (3H, s, H_3-2′); ^{13}C NMR (acetone-d_6, 150 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 170.1 (C-1′), 21.5 (C-2′); (+)-ESIMS *m*/*z* 399 $[M + Na]^+$; (+)-HRESIMS *m*/*z* 399.2151 $[M + Na]^+$ (calcd for $C_{22}H_{32}O_5Na$, 399.2142).

*(+)-(12E,2S,3S,4R,5R,6R,9S,11S,15R)-3-Cinnamoyloxy-5,6-epoxylathyr-12-en-15-ol-14-one (**4**):* white, amorphous powder; $[\alpha]^{20}_D$ +82.8 (*c* 0.48, MeOH); UV(MeOH) λ_{max} (log ε) 205 (2.33), 217 (2.36), 273 (2.64) nm; CD (MeOH) 257 ($\Delta\varepsilon$ −4.31), 286 ($\Delta\varepsilon$ +6.16) nm; IR ν_{max} 3466, 3061, 2958, 2931, 2873, 1715, 1634, 1496, 1452, 1379, 1310, 1279, 1203, 1174, 1148, 1076, 1053, 988, 907, 866, 810, 768, 710, 685, 565 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 1, for the acyl unit δ 7.67 (2H, m, H-2′/6′), 7.45 (2H, m, H-3′/5′), 7.43 (1H, m, H-4′), 7.75 (1H, d, *J* = 16.5 Hz, H-7′), 6.66 (1H, d, *J* = 16.5 Hz, H-8′); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 135.6 (C-1′), 129.0 (C-2′/6′), 129.8 (C-3′/5′), 131.0 (C-4′), 145.1 (C-7′), 119.5 (C-8′), 166.4 (C-9′); (+)-ESIMS *m*/*z* 465 $[M + H]^+$, 487 $[M + Na]^+$, 503 $[M + K]^+$; (+)-HRESIMS *m*/*z* 487.2483 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_5Na$, 487.2461).

*(−)-(12E,2S,3S,4R,5R,6R,9S,11S,15R)-3,15-Dibenzoyloxy-5,6-epoxylathyr-12-en-14-one (**5**):* white, amorphous powder; $[\alpha]^{20}_D$ −13.4 (*c* 0.32, MeOH); UV (MeOH) λ_{max} (log ε) 273 (7.23), 230 (7.51), 201 (7.65) nm; CD (MeOH) 204 ($\Delta\varepsilon$ +1.23), 223 ($\Delta\varepsilon$ −2.31), 243 ($\Delta\varepsilon$ +4.09), 271 ($\Delta\varepsilon$ +6.31), 318 ($\Delta\varepsilon$ −0.58) nm; IR ν_{max} 2995, 2970, 2948, 2931, 2875, 1720, 1659, 1624, 1452, 1378, 1290, 1278, 1272, 1114, 858, 710 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 1, for the acyl unit δ 8.21 (1H, d, *J* = 7.5 Hz, H-2′/6′), 7.60 (1H, t, *J* = 7.5 Hz, H-3′/5′), 7.43 (1H, t, *J* = 7.5 Hz, H-4′), 8.13 (2H, d, *J* = 7.5 Hz, H-2″/6″), 7.42 (2H, t, *J* = 7.5 Hz, H-3″/5″), 7.63 (1H, t, *J* = 7.5 Hz, H-4″); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 130.9 (C-1′), 130.4 (C-2′/6′), 130.5 (C-3′/5′), 134.0 (C-4′), 165.8 (C-7′), 131.2 (C-1″), 130.5 (C-2″/6″), 129.9 (C-3″/5″), 134.8 (C-4″), 165.5 (C-7″); (+)-ESIMS *m*/*z* 565 $[M + Na]^+$; (+)-HRESIMS *m*/*z* 565.2546 $[M + Na]^+$ (calcd for 565.2561).

*(+)-(12E,2S,3S,4R,5R,6R,9S,11S,15R)-3-Benzoyloxy-5,6-epoxylathyr-12-en-15-ol-14-one (**6**):* white, amorphous powder; $[\alpha]^{20}_D$ +22.7 (*c* 0.22, MeOH); UV (MeOH) λ_{max} (log ε) 201 (4.75), 229 (4.81), 270 (4.73) nm; CD (MeOH) 211 ($\Delta\varepsilon$ +0.51), 229 ($\Delta\varepsilon$ −3.13), 270 ($\Delta\varepsilon$ +3.47) nm; IR ν_{max} 3459, 2927, 2857, 1717, 1613, 1452, 1381, 1354, 1315, 1269, 1177, 1148, 1112, 1067, 1027, 998, 938, 906, 861, 808, 784, 711, 568 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 1, for the acyl unit δ 8.14 (2H, d, *J* = 7.5 Hz, H-2′/6′), 7.51 (2H, t, *J* = 7.5 Hz, H-3′/5′), 7.63 (1H, t, *J* = 7.5 Hz, H-4′);

^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 131.6 (C-1′), 130.4 (C-2′/6′), 129.4 (C-3′/5′), 133.7 (C-4′), 166.1 (C-7′); (+)-ESIMS m/z 439 $[M + H]^+$, 461 $[M + Na]^+$, 477 $[M + K]^+$, 899 $[2\,M + Na]^+$; (+)-HRESIMS m/z 461.2316 $[M + Na]^+$ (calcd for $C_{27}H_{34}O_5Na$, 461.2304).

*(−)-(12E,2S,3S,4R,5R,6R,9S,11S,15R)-3-Acetoxy-15-benzoyloxy-5,6-epoxylathyr-12-en-14-one (**7**):* white, amorphous powder; $[\alpha]^{20}_D$ −94.3 (*c* 0.56, MeOH); UV (MeOH) λ_{max} (log ε) 201 (2.31), 235 (2.37), 272 (2.24) nm; CD (MeOH) 240 ($\Delta\varepsilon$ −3.44), 273 ($\Delta\varepsilon$ +3.61), 316 ($\Delta\varepsilon$ −1.13) nm; IR ν_{max} 3065, 2932, 2873, 1721, 1655, 1625, 1493, 1452, 1374, 1315, 1276, 1234, 1211, 1180, 1149, 1106, 1062, 1022, 929, 902, 856, 805, 778, 714, 687, 605, 570, 531 cm^{-1}; ^{1}H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 1, for the acyl units δ 8.12 (2H, d, *J* = 7.5 Hz, H-2′/6′), 7.55 (2H, t, *J* = 7.5 Hz, H-3′/5′), 7.68 (1H, t, *J* = 7.5 Hz, H-4′), 2.08 (3H, s, H$_3$-2″); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl units δ 131.2 (C-1′), 130.4 (C-2′/6′), 129.8 (C-3′/5′), 134.5 (C-4′), 165.6 (C-7′), 170.3 (C-1″), 20.8 (C-2″); (+)-ESIMS m/z 481 $[M + H]^+$, 503 $[M + Na]^+$, 519 $[M + K]^+$; (+)-HRESIMS m/z 503.2396 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_6Na$, 503.2404).

Alkaline Hydrolysis of 1−7. Compounds **1**−**7** (1.0−5.2 mg) were dissolved separately in 95% EtOH (1 mL); then aqueous NaOH (0.5 mL, 1 mol/L) was added to each, and the solution was stirred at rt for 24 h. The reaction solutions were evaporated to dryness under reduced pressure. The residues were dissolved in EtOAc, and TLC indicated the presence of an identical product in the residues. The product was separated by PTLC using petroleum ether−EtOAc (3:1) and identified as (−)-(12*E*,2*S*,3*S*,4*R*,5*R*,6*R*,9*S*,11*S*,15*R*)-5,6-epoxylathyr-12-ene-3,15-diol-14-one[13] on the basis of the following data (absent in the literature): white, amorphous solid; $[\alpha]^{20}_D$ −22.0 (*c* 0.12, MeOH); CD (MeOH) 196 ($\Delta\varepsilon$ −4.98), 215 ($\Delta\varepsilon$ +1.05), 275 ($\Delta\varepsilon$ +1.01), 313 ($\Delta\varepsilon$ −0.78), 352 ($\Delta\varepsilon$ +0.25) nm; ^{1}H NMR (acetone-d_6, 500 MHz) δ 3.12 (1H, dd, *J* = 13.0 and 7.0 Hz, H-1a), 1.62 (1H, t, *J* = 13.0 Hz, H-1b), 1.97 (1H, m, H-2), 3.94 (1H, br s, H-3), 1.62 (1H, m, H-4), 3.42 (1H, d, *J* = 9.0 Hz, H-5), 1.95 (1H, m, H-7a), 1.42 (1H, m, H-7b), 1.72 (1H, m, H-8a), 1.62 (1H, m, H-8b), 1.26 (1H, dd, *J* = 12.0 and 8.0 Hz, H-9), 1.62 (1H, dd, *J* = 11.5 and 8.0 Hz, H-11), 7.87 (1H, d, *J* = 11.5 Hz, H-12), 1.03 (3H, d, *J* = 7.5 Hz, H$_3$-16), 1.11 (3H, s, H$_3$-17), 1.19 (3H, s, H$_3$-18), 1.07 (3H, s, H$_3$-19), 1.79 (3H, s, H$_3$-20); ^{13}C NMR (acetone-d_6, 125 MHz) δ 46.9 (C-1), 30.6 (C-2), 79.3 (C-3), 53.4 (C-4), 59.3 (C-5), 63.3 (C-6), 40.0 (C-7), 23.8 (C-8), 35.0 (C-9), 26.4 (C-10), 39.4 (C-11), 148.2 (C-12), 134.2 (C-13), 199.0 (C-14), 89.2 (C-15), 14.1 (C-16), 20.5 (C-17), 29.1 (C-18), 16.5 (C-19), 12.7 (C-20).

*(−)-(5E,12E,2S,3S,4S,9S,11S,15R)-3,15-Diacetoxylathyra-5,12-dien-14-one (**8**):* colorless needles (MeOH), mp 155−156 °C; $[\alpha]^{20}_D$ −10.8 (*c* 0.28, MeOH); UV (MeOH) λ_{max} (log ε) 205 (4.90), 276 (5.07) nm; CD (MeOH) 219 ($\Delta\varepsilon$ −13.12), 240 ($\Delta\varepsilon$ −11.73), 278 ($\Delta\varepsilon$ +11.06) nm; IR (KBr) ν_{max} 2980, 2918, 1732, 1697, 1648, 1621, 1436, 1380, 1249, 1193, 1145, 1126, 1065, 1036, 987, 959, 937, 895, 867, 803, 772, 740, 725, 630, 609, 585, 552, 536 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) data for the diterpene moiety, see Table 1, for the acyl units δ 2.02 (3H, s, H$_3$-2′), 2.13 (3H, s, H$_3$-2″); ^{13}C NMR ($CDCl_3$, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl units δ 169.6 (C-1′), 21.4 (C-2′), 170.6 (C-1″), 20.9 (C-2″); (+)-ESIMS m/z 425 $[M + Na]^+$, 441 $[M + K]^+$; (−)-ESIMS m/z 401 $[M - H]^+$; (+)-HRESIMS m/z 425.2309 $[M + Na]^+$ (calcd for $C_{24}H_{34}O_5Na$, 425.2304).

*(+)-(5E,12E,2S,3S,4S,9S,11S,15R)-3-Cinnamoyloxylathyra-5,12-dien-15-ol-14-one (**9**):* white, amorphous powder; $[\alpha]^{20}_D$ +70.3 (*c* 0.17, MeOH); UV (MeOH) λ_{max} (log ε) 195 (2.01), 216 (2.19), 277 (2.38) nm; CD (MeOH) 202 ($\Delta\varepsilon$ +0.76), 221 ($\Delta\varepsilon$ −4.32), 231 ($\Delta\varepsilon$ −3.15), 249 ($\Delta\varepsilon$ −5.41), 288 ($\Delta\varepsilon$ +6.74) nm; IR ν_{max} 3466, 3061, 2923, 2857, 1712, 1636, 1611, 1496, 1451, 1378, 1357, 1309, 1265, 1202, 1170, 1138, 1055, 985, 931, 903, 864, 810, 767, 710, 684, 606, 567 cm^{-1}; ^{1}H NMR (acetone-d_6, 600 MHz) data for the diterpene moiety, see Table 2, for the acyl unit δ 7.67 (2H, m, H-2′/6′), 7.44 (2H, m, H-3′/5′), 7.44 (1H, m, H-4′), 7.74 (1H, d, *J* = 16.2 Hz, H-7′), 6.71 (1H, d, *J* = 16.2 Hz, H-8′); ^{13}C NMR (acetone-d_6, 150 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 135.6 (C-1′), 129.0 (C-2′/6′), 129.8 (C-3′/5′), 131.1 (C-4′), 145.3 (C-7′), 119.4 (C-8′), 166.8 (C-9′); (+)-ESIMS m/z 449 $[M + H]^+$, 471 $[M + Na]^+$, 487 $[M + K]^+$; (+)-HRESIMS m/z 471.2557 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_4Na$, 471.2511).

*(−)-(5E,12E,2S,3S,4S,9S,11S,15R)-15-Cinnamoyloxylathyra-5,12-dien-3-ol-14-one (**10**):* colorless needles (MeOH), mp 100−102 °C; $[\alpha]^{20}_D$ −118.1 (*c* 0.46, MeOH); UV (MeOH) λ_{max} (log ε) 206 (2.45), 217 (242), 276 (2.68) nm; CD (MeOH) 225 ($\Delta\varepsilon$ −5.06), 257 ($\Delta\varepsilon$ −6.95), 295 ($\Delta\varepsilon$ +5.69) nm; IR ν_{max} 3482, 3060, 2922, 2872, 1711, 1635, 1616, 1578, 1496, 1451, 1378, 1332, 1313, 1275, 1203, 1169, 1119, 1056, 1031, 1007, 984, 926, 902, 863, 769, 712, 685, 615, 588, 539 cm^{-1}; ^{1}H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 2, for the acyl unit δ 7.66 (2H, m, H-2′/6′), 7.43 (2H, m, H-3′/5′), 7.43 (1H, m, H-4′), 7.66 (1H, d, *J* = 16.0 Hz, H-7′), 6.58 (1H, d, *J* = 16.0 Hz, H-8′); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 135.3 (C-1′), 129.0 (C-2′/6′), 129.8 (C-3′/5′), 131.3 (C-4′), 146.0 (C-7′), 119.5 (C-8′), 166.0 (C-9′); (+)-ESIMS m/z 449 $[M + H]^+$, 471 $[M + Na]^+$, 487 $[M + K]^+$, 919 $[2\,M + Na]^+$; (+)-HRESIMS m/z 471.2518 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_4Na$, 471.2506).

*(−)-(5E,12E,2S,3S,4S,9S,11S,15R)-15-Benzoyloxylathyra-5,12-dien-3-ol-14-one (**11**):* white prisms (EtOAc); mp 198−200 °C; $[\alpha]^{20}_D$ −132.9 (*c* 0.10, MeOH); UV (MeOH) λ_{max} (log ε) 279 (4.00), 234 (4.15), 201(4.36) nm; CD (MeOH) 241 ($\Delta\varepsilon$ −26.29), 283 ($\Delta\varepsilon$ +16.63) nm; IR ν_{max} 3576, 2943, 2923, 2859, 1708, 1643, 1613, 1453, 1325, 1315, 1297, 1280, 1268, 1223, 1146, 1117, 1071, 1058, 1027, 998, 985, 902, 863, 715 cm^{-1}; ^{1}H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 2, for the acyl unit δ 8.03 (2H, d, *J* = 8.0 Hz, H-2′/6′), 7.51 (2H, t, *J* = 8.0 Hz, H-3′/5′), 7.52 (1H, t, *J* = 8.0 Hz, H-4′); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 131.7 (C-1′), 130.3 (C-2′/6′), 129.4 (C-3′/5′), 134.1 (C-4′), 165.6 (C-7′); (+)-ESIMS m/z 445 $[M + Na]^+$; (+)-HRESIMS m/z 445.2340 $[M + Na]^+$ (calcd for 445.2349).

Alkaline Hydrolysis of 8−11. Compounds **8**−**11** (0.5−6.0 mg) were dissolved separately in 95% EtOH (1.0−2.0 mL); then aqueous NaOH (0.5−1.0 mL, 1.0 mol/L) was added in each, and the solutions were stirred at rt for 24 h. The reaction solutions were evaporated to dryness under reduced pressure. The residues were dissolved in EtOAc, and TLC indicated an identical product in the residues. The product was separated by PTLC using petroleum ether−EtOAc (3:1) as the mobile phase and identified as (+)-(5*E*,12*E*,2*S*,3*S*,4*S*,9*S*,11*S*,15*R*)-lathyra-5,12-diene-3,15-diol-14-one[13] on the basis of the following data (absent in the literature): white, amorphous solid; $[\alpha]^{20}_D$ +85.6 (*c* 0.06, MeOH); CD (MeOH) 198 ($\Delta\varepsilon$ +5.49), 249 ($\Delta\varepsilon$ −14.61), 285 ($\Delta\varepsilon$ +9.15), 335 ($\Delta\varepsilon$ +2.36) nm; ^{1}H NMR (acetone-d_6, 500 MHz) δ 3.28 (1H, dd, *J* = 13.0 and 9.0 Hz, H-1a), 1.73 (1H, t, *J* = 13.0 Hz, H-1b), 2.14 (1H, m, H-2), 3.88 (1H, m, H-3), 2.57 (1H, br d, *J* = 11.0 Hz, H-4), 5.76 (1H, d, *J* = 11.0 Hz, H-5), 2.19 (1H, m, H-7a), 1.44 (1H, m, H-7b), 1.86 (1H, m, H-8a), 1.57 (1H, m, H-8b), 1.10 (1H, m, H-9), 1.50 (1H, m, H-11), 7.50 (1H, d, *J* = 12.0 Hz, H-12), 1.05 (3H, d, *J* = 7.0 Hz, H$_3$-16), 1.42 (3H, s, H$_3$-17), 1.16 (3H, s, H$_3$-18), 1.04 (3H, s, H$_3$-19), 1.79 (3H, s, H$_3$-20); ^{13}C NMR (acetone-d_6, 125 MHz) δ 46.2 (C-1), 39.7 (C-2), 80.7 (C-3), 53.8 (C-4), 122.8 (C-5), 140.4 (C-6), 37.3 (C-7), 29.8 (C-8), 35.0 (C-9), 24.7 (C-10), 30.3 (C-11), 150.5 (C-12), 132.4 (C-13), 198.6 (C-14), 92.6 (C-15), 14.7 (C-16), 20.9 (C-17), 28.9 (C-18), 16.4 (C-19), 12.6 (C-20).

*(−)-(6Z,12E,2S,3S,4R,5R,9S,11S,15R)-3-Cinnamoyloxylathyra-6,12-diene-5,15-diol-14-one (**12**):* colorless needles (acetone); mp 85−87 °C; $[\alpha]^{20}_D$ −57.2 (*c* 0.36, MeOH); UV (MeOH) λ_{max} (log ε) 196 (2.39), 216

(256), 278 (2.68) nm; CD (MeOH) 211 ($\Delta\varepsilon$ +0.32), 223 ($\Delta\varepsilon$ −2.25), 229 ($\Delta\varepsilon$ −2.21), 267 ($\Delta\varepsilon$ −10.88), 295 ($\Delta\varepsilon$ +3.91) nm; IR ν_{max} 3432, 3063, 2927, 2870, 1694, 1615, 1495, 1451, 1377, 1330, 1308, 1273, 1202, 1169, 1050, 1003, 982, 928, 906, 867, 767, 709, 683, 564 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 2, for the acyl unit δ 7.66 (2H, m, H-2′/6′), 7.43 (2H, m, H-3′/5′), 7.43 (1H, m, H-4′), 7.70 (1H, d, J = 16.0 Hz, H-7′), 6.75 (1H, d, J = 16.0 Hz, H-8′); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 135.7 (C-1′), 128.9 (C-2′/6′), 129.8 (C-3′/5′), 131.0 (C-4′), 144.8 (C-7′), 120.1 (C-8′), 166.5 (C-9′); (+)-ESIMS m/z 487 $[M + Na]^+$; (+)-HRESIMS m/z 487.2491 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_5Na$, 487.2461).

*(−)-(6Z,12E,2S,3S,4R,5R,9S,11S,15R)-5-Cinnamoyloxylathyra-6,12-diene-3,15-diol-14-one (**13**):* white, amorphous powder; $[\alpha]^{20}_D$ −89.3 (c 0.10, MeOH); UV (MeOH) λ_{max} (log ε) 278 (4.00), 202 (4.00) nm; CD (MeOH) 273 ($\Delta\varepsilon$ −6.96), 344 ($\Delta\varepsilon$ +0.14) nm; IR ν_{max} 3429, 2932, 2872, 1713, 1637, 1620, 1451, 1378, 1335, 1304, 1276, 1203, 1169, 1083, 1066, 1050, 1004, 984, 930, 907, 896, 768, 712, 685 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 2, for the acyl unit δ 7.65 (2H, m, H-2′/6′), 7.43 (2H, m, H-3′/5′), 7.42 (1H, m, H-4′), 7.64 (1H, d, J = 16.0 Hz, H-7′), 6.50 (1H, d, J = 16.0 Hz, H-8′); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl unit δ 135.2 (C-1′), 128.6 (C-2′/6′), 129.4 (C-3′/5′), 130.1 (C-4′), 144.2 (C-7′), 119.2 (C-8′), 165.4 (C-9′); (+)-ESIMS m/z 487 $[M + Na]^+$; (+)-HRESIMS m/z 487.2476 $[M + Na]^+$ (calcd for 487.2455).

*(−)-(6Z,12E,2S,3S,4R,5R,9S,11S,15R)-3-Acetoxy-15-benzoyloxylathyra-6,12-dien-5-ol-14-one (**14**):* white, amorphous powder; $[\alpha]^{20}_D$ −101.2 (c 0.07, MeOH); UV (MeOH) λ_{max} (log ε) 202 (2.42), 232 (2.30), 281 (2.02) nm; CD (MeOH) 220 ($\Delta\varepsilon$ −4.64), 238 ($\Delta\varepsilon$ −7.53), 280 ($\Delta\varepsilon$ +1.82), 312 ($\Delta\varepsilon$ −1.54) nm; IR ν_{max} 3480, 3363, 2923, 2853, 1720, 1649, 1630, 1453, 1374, 1315, 1281, 1242, 1150, 1107, 1067, 1025, 927, 870, 715, 643, 606, 577 cm^{-1}; ^1H NMR (acetone-d_6, 600 MHz) data for the diterpene moiety, see Table 2, for the acyl units δ 8.20 (2H, d, J = 7.8 Hz, H-2′/6′), 7.56 (2H, t, J = 7.8, H-3′/5′), 7.68 (1H, t, J = 7.8 Hz, H-4′), 2.14 (3H, s, H_3-2″); ^{13}C NMR (acetone-d_6, 150 MHz) data for the diterpene moiety, see Table 3, for the acyl units δ 132.0 (C-1′), 130.7 (C-2′/6′), 129.5 (C-3′/5′), 134.4 (C-4′), 165.9 (C-7′), 170.5 (C-1″), 21.3 (C-2″); (+)-ESIMS m/z 503 $[M + Na]^+$, 519 $[M + K]^+$; (+)-HRESIMS m/z 503.2414 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_6Na$, 503.2410).

*(−)-(6Z,12E,2S,3S,4R,5R,9S,11S,15R)-5-Acetoxy-15-benzoyloxylathyra-6,12-dien-3-ol-14-one (**15**):* colorless needles (acetone); mp 162−163 °C, $[\alpha]^{20}_D$ −109.9 (c 0.19, MeOH); UV (MeOH) λ_{max} (log ε) 202 (2.54), 234 (2.46), 278 (2.28) nm; CD (MeOH) 220 ($\Delta\varepsilon$ −2.82), 232 ($\Delta\varepsilon$ −2.43), 244 ($\Delta\varepsilon$ −2.68), 277 ($\Delta\varepsilon$ +1.02), 319 ($\Delta\varepsilon$ −2.27) nm; IR ν_{max} 3559, 3059, 3026, 2921, 2856, 1721, 1698, 1652, 1627, 1493, 1452, 1370, 1315, 1281, 1244, 1211, 1149, 1105, 1066, 1013, 961, 921, 872, 838, 779, 717, 690, 640, 602, 575 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 2, for the acyl units δ 8.18 (2H, d, J = 7.5 Hz, H-2′/6′), 7.51 (2H, t, J = 7.5 Hz, H-3′/5′), 7.65 (1H, t, J = 7.5 Hz, H-4′), 2.01 (3H, s, H_3-2″); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for the acyl units δ 131.8 (C-1′), 131.0 (C-2′/6′), 129.3 (C-3′/5′), 134.2 (C-4′), 165.8 (C-7′), 169.8 (C-1″), 21.3 (C-2″); (+)-ESIMS m/z 481 $[M + H]^+$, 503 $[M + Na]^+$, 519 $[M + K]^+$; (+)-HRESIMS m/z 519.2189 $[M + K]^+$ (calcd for $C_{29}H_{36}O_6K$, 519.2149).

Alkaline Hydrolysis of 12−15. Compounds **12**−**15** (0.6−1.8 mg) were dissolved separately in 95% EtOH (0.5 mL); then aqueous NaOH aqueous (0.2 mL, 1 mol/L) was added in each and stirred at rt for 24 h. The reaction solutions were evaporated to dryness, and the residues were dissolved with EtOAc. TLC indicated an identical product in the residues. The product was separated by PTLC using petroleum ether−EtOAc (2:1) and identified as (−)-(6*Z*,12*E*,2*S*,3*S*,4*R*,5*R*,9*S*,11*S*,-15*R*)-lathyra-6,12-diene-3,5,15-triol-14-one by the following data: white, amorphous solid; $[\alpha]^{20}_D$ −126.3 (c 0.03, MeOH); ^1H NMR (acetone-d_6, 500 MHz) δ 3.09 (1H, dd, J = 13.5 and 10.5 Hz, H-1a), 1.62 (1H, dd, J = 13.5 and 10.5 Hz, H-1b), 2.20 (1H, m, H-2), 4.39 (1H, br s, H-3), 2.40 (1H, m, H-4), 5.25 (1H, d, J = 8.0 Hz, H-5), 5.01 (1H, dd, J = 12.0 and 2.0 Hz, H-7), 2.20 (1H, m, H-8a), 2.06 (1H, m, H-8b), 1.18 (1H, m, H-9), 1.52 (1H, dd, J = 11.0 and 8.5 Hz, H-11), 7.70 (1H, d, J = 11.5 Hz, H-12), 1. 06 (3H, d, J = 6.5 Hz, H_3-16), 1.48 (3H, s, H_3-17), 1.14 (3H, s, H_3-18), 1.23 (3H, s, H_3-19), 1.65 (3H, s, H_3-20); ^{13}C NMR (acetone-d_6, 125 MHz) δ 49.9 (C-1), 37.6 (C-2), 80.1 (C-3), 56.9 (C-4), 64.9 (C-5), 136.7 (C-6), 125.4 (C-7), 24.1 (C-8), 31.3 (C-9), 24.8 (C-10), 28.3 (C-11), 148.5 (C-12), 134.5 (C-13), 200.7 (C-14), 90.7 (C-15), 14.8 (C-16), 18.3 (C-17), 28.5 (C-18), 16.3 (C-19), 12.2 (C-20).

*(−)-(6Z,12E,2S,3S,4R,5R,9S,11S,15R)-15-Cinnamoyloxy-3,5-di-O-isopropylidenelathyra-6,12-dien-14-one (**16**):* yellowish oil; $[\alpha]^{20}_D$ −59.0 (c 0.12, MeOH); UV (MeOH) λ_{max} (log ε) 275 (3.87), 219 (3.72), 201 (3.89) nm; IR ν_{max} 3003, 2984, 2926, 2880, 2856, 1715, 1663, 1638, 1630, 1452, 1378, 1316, 1264, 1231, 1220, 1167, 1128, 1064, 1036, 982, 923, 892, 766, 685 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) data for the diterpene moiety, see Table 2, for the substituents δ 7.69 (2H, m, H-2′/6′), 7.44 (2H, m, H-3′/5′), 7.43 (1H, m, H-4′), 7.68 (1H, d, J = 16.5 Hz, H-7′), 6.78 (1H, d, J = 16.5 Hz, H-8′), 1.29 (3H, s, H_3-1″), 1.53 (3H, s, H_3-3″); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 3, for for the substituents δ 135.1 (C-1′), 129.2 (C-2′/6′), 129.8 (C-3′/5′), 131.5 (C-4′), 146.6 (C-7′), 119.0 (C-8′), 166.1 (C-9′), 26.8 (C-1″), 99.8 (C-2″), 24.8 (C-3″); (+)-ESIMS m/z 527 $[M + Na]^+$; (+)-HRESIMS m/z 527.2772$[M + Na]^+$ (calcd for 527.2768).

*(+)-(12E,2S,3S,4R,5R,9S,11S,15R)-15-Cinnamoyloxy-lathyra-6(17),12-diene-3,5-diol-14-one (**17**):* colorless needles (acetone); mp 89−91 °C, $[\alpha]^{20}_D$ +4.9 (c 0.16, MeOH); UV (MeOH) λ_{max} (log ε) 218 (1.84), 276 (2.12) nm; CD (MeOH) 201 ($\Delta\varepsilon$ −7.67), 250 ($\Delta\varepsilon$ +0.49), 259 ($\Delta\varepsilon$ +0.34), 289 ($\Delta\varepsilon$ +8.42), 325 ($\Delta\varepsilon$ −1.26) nm; IR ν_{max} 3466, 3062, 2925, 2871, 1712, 1632, 1578, 1496, 1450, 1427, 1377, 1332, 1314, 1270, 1202, 1165, 1156, 1129, 1063, 1038, 1015, 990, 903, 862, 768, 712, 685, 616, 575 cm^{-1}; ^1H NMR (acetone-d_6, 600 MHz) data for the diterpene moiety, see Table 2, for the acyl unit δ 7.69 (2H, m, H-2′/6′), 7.43 (2H, m, H-3′/5′), 7.43 (1H, m, H-4′), 7.69 (1H, d, J = 15.6 Hz, H-7′), 6.72 (1H, d, J = 15.6 Hz, H-8′); ^{13}C NMR (acetone-d_6, 125 MHz) data for the diterpene moiety, see Table 1, for the acyl unit δ 135.3 (C-1′), 129.1 (C-2′/6′), 129.8 (C-3′/5′), 131.4 (C-4′), 146.3 (C-7′), 119.5 (C-8′), 166.1 (C-9′); (+)-ESIMS m/z 465 $[M + H]^+$, 487 $[M + Na]^+$, 503 $[M + K]^+$; (+)-HRESIMS m/z 487.2481 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_5Na$, 487.2455).

Anti-HIV Activity Assay. See ref 21.

Vasodilating Activity Assays. See ref 22.

Cells, Culture Conditions, and Cell Proliferation Assay. See ref 18.

Antioxidative Activity Assay. See ref 19.

PTP1B Inhibition Assay. See ref 20.

■ ASSOCIATED CONTENT

Supporting Information. Tables of atomic coordinates and equivalent isotropic displacement parameters for the oxygen and carbon atoms; bond lengths; and bond angles for **1**. Crystal cell diagram for **1**. Copies of MS, IR, CD, and 1D and 2D NMR spectra of **1**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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