*Journal of Natural Products*
*Vol. 58, No. 12, pp. 1883-1888, December 1995*



# FOUR ESTERS OF A NEW PENTACYCLIC DITERPENOID OF THE MYRSINOL TYPE FROM *EUPHORBIA ALEPPICA*

LI YANG, YAN-PING SHI, ZHONG-JIAN JIA,* SADIQ SALEH,[1] and JAMIL LAHHAM[1]

*Institute of Organic Chemistry, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China*

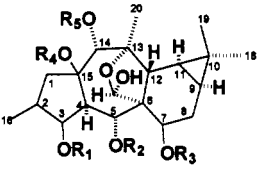
ABSTRACT.—Four new pentacyclic polyfunctional diterpenes, euphoppins A–D [**1–4**], were isolated from whole plants of *Euphorbia aleppica*. Their structures were established by spectral methods as tetra esters [**1–3**] and a penta ester [**4**] of a hitherto unknown polyfunctional pentacyclic diterpene parent alcohol, structurally related to myrsinol.

Plants of the genus *Euphorbia* are known to produce a variety of diterpenoids (1,2), some of which are highly irritant and have tumor-promoting activity while others exhibit cytotoxic activity (3,4). We have reported previously the isolation and structural determination of several new diterpenoids from *Euphorbia* spp. from the western People's Republic of China which are used in Chinese folk medicine as antitumor agents (5–9). However, no investigation of *E. aleppica* L. (Euphorbiaceae), indigenous to Jordan, has yet been published. We now report herein the isolation, characterization, and structural elucidation of four new diterpene esters, euphoppins A–D [**1–4**], from a petroleum ether (60–90°)-$Et_2O$-MeOH (1:1:1) extract *E. aleppica* collected in Jordan.

Euphoppin A [**1**], obtained as a colorless gum, displayed ir absorptions characteristic of hydroxyl, carbonyl, and alkene functionalities at 3464, 1740, and 1651 $cm^{-1}$, respectively. Fabms and elemental analysis established a molecular formula of $C_{31}H_{44}O_{11}$ for the compound. The $^1H$- and $^{13}C$-nmr spectra of **1** indicated the presence of three acetoxyl groups ($\delta_H$ 2.04, 2.03, 1.79; $\delta_C$ 21.29, 171.72, 21.03, 170.74, 22.92, 169.65) and a tigloyl group ($\delta_H$ 6.76, 1.79, 1.77; $\delta_C$ 165.46, 128.97, 137.98, 14.53, 11.92), which were supported by the ms fragment ions at *m/z* 575 $[MH-H_2O]^+$, 475 $[575-\text{tiglic acid}]^+$, 415 $[475-HOAc]^+$, 355 $[475-2\times HOAc]^+$, 295 $[475-3\times HOAc]^+$, 83 $[\text{tigloyl}]^+$, and 43 $[Ac]^+$. Apart from the signals of the ester groups, the $^1H$-nmr spectrum of **1** showed signals for a secondary methyl group ($\delta$ 0.79) and three tertiary methyl groups ($\delta$ 0.97, 1.04, 1.51) as well as five oxymethine protons at $\delta$ 5.78 (d), 5.55 (s), 5.14 (dd), 4.99 (t), and 4.15 (s). A combination of $^{13}C$- and DEPT nmr spectra revealed that the basic carbon skeleton of **1** (exclusive of three acetates and one tigloyl group) consisted of four methyl, two methylene, ten methine (five oxymethine), and four quaternary carbons (two carboxy). Among the 20 carbons, there were no $sp^2$ carbon atoms. Based upon ten degrees of unsaturation ($C_{31}H_{44}O_{11}$), a pentacyclic diterpenoid skeleton ($C_{20}H_{26}O$) was proposed for **1**, with five degrees of unsaturation accounted for by three acetates and one tigloyl substituent. In addition, a cyclopropane ring including a quaternary carbon (C-10) bearing *gem*-dimethyl groups was indicated by the upfield signals in the $^1H$- and $^{13}C$-nmr spectra [$\delta_H$ 0.86, 0.91, each 1H, m; $\delta_C$ 19.15 (C), 18.77 (CH), 23.82 (CH)].

Two-dimensional nmr experiments ($^1H$-$^1H$ COSY and $^{13}C$-$^1H$ COSY) showed four main fragments for **1**, separated by quaternary carbons: $CH_2$-CH($CH_3$)-CH ($OR^1$)-CH-CH ($OR^2$), CH ($OR^3$)-$CH_2$-CH-CH-CH, CH ($OR^5$), and CH (O) (OH). The C-H and H-H interconnectivity of these fragments was established through $^{13}C$-$^1H$ COLOC experi-

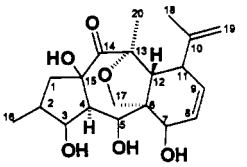
[1]Chemistry and Biological Sciences Departments, Yarmouk University, Irbid, Jordan.



**1** $R^1=R^2=R^4=-COCH_3$, $R^3=-$Tiglate, $R^5=-H$
**2** $R^1=R^2=-COCH_3$, $R^3=R^4=-$Tiglate, $R^5=-H$
**3** $R^1=R^2=-COCH_3$, $R^3=-$Tiglate, $R^4=-COC_6H_5$, $R^5=H$
**4** $R^1=R^2=R^5=-COCH_3$, $R^3=R^4=-$Tiglate
**5** $R^1=R^2=R^3=R^4=R^5=-H$ (Parent alcohol)

ments. Analysis of these 2D nmr experiments and a comparison of the data obtained with spectral data for myrsinol [**6**] and its derivatives (10,11), indicated that **1** was based on a pentacyclic diterpenoid with a cyclopropane ring, two five-membered rings, and a six- and seven-membered ring. The only difference between the parent alcohol [**5**] of **1** and the tetracyclic 14-deoxo-14-hydroxylmyrsinol (10) was the fifth ring in **1**, which was shown to be a 9,10,11-cyclopropane instead of the 11-isopropenyl substituent in myrsinol [**6**] (together with a $\Delta^{8,9}$ double bond). Because of the presence of the fifth ring, **1** was confirmed as a novel tetraester of a hitherto unknown polyfunctional pentacyclic diterpene parent alcohol, structurally related to myrsinol [**6**].

Conclusive evidence for the location of the various ester functions and assignments of the $^{13}$C-nmr resonances of the ester groups was provided by a 2D long-range $^1$H-$^{13}$C nmr shift-correlated spectrum ($^1$H-$^{13}$C COLOC). The four ester carbonyls (δ 170.74, 171.72, 165.46, 169.65) were easily distinguishable by their chemical shifts. The carbonyl at $\delta_C$ 170.74 correlated with the methyl group



**6**

at $\delta_H$ 2.04 and with H-3 ($\delta_H$ 4.99), indicating that it was attached to the oxygen at C-3. Similarly, correlation of the carbonyl at $\delta_C$ 171.72 with the methyl group at $\delta_H$ 1.79 and with H-5 ($\delta_H$ 5.78) established substitution at C-5, while the functionality at C-7 was established by correlations of the carbonyl at δ 165.46 with the tigloyl signals ($\delta_H$ 6.76, 1.77, 1.79) and also with H-7 ($\delta_H$ 5.14). These observations unambiguously assigned the ester attachments in **1**. Furthermore, the lack of a correlation of the carbonyl at $\delta_C$ 169.65 to an oxymethine defined the ester attachment to the oxygen at C-15. Based on the chemical shift and NOESY data obtained, assignment of the two secondary hydroxyl groups attached to C-14 and C-17 was straightforward.

The coupling constants of H-1, H-3, H-4, and H-5 in **1** ($J_{1\alpha,2}$=8.4 Hz, $J_{1\beta,2}=J_{2,3}=J_{3,4}$=3.1 Hz, $J_{4,5}$=10.7 Hz) were similar or identical to those reported for enukolurin (12), kansuinine B (13), esulone A (14), and the jolkinols (15). Therefore, the configuration of **1** at C-2 to C-5, and C-15 must be identical to these model compounds. Furthermore, the relative configurations of the other chiral centers in **1** could be deduced by the correlations in the $^1$H-$^1$H NOESY spectrum (Table 3). Since cross-peaks could be identified between the proton pairs (H-5/H-12, H-12/H-14, H-12/H-19, H-14/H-20, H-7/H-9, H-4/H-17) then H-5, H-12, H-14, H-19, and H-20 must lie on the same side of the molecular plane (i.e., they have the same orientation), while H-7 and H-9, together with

H-4 and H-17, are on the opposite side, as shown in Figure 1. Consequently, **1** was confirmed as the 3,5,15-triacetate-7-tiglate of the polyfunctional parent alcohol **5**.

Euphoppin B [**2**], obtained as a colorless gum, showed ir absorptions at 3460 (OH), 1720 (CO), and 1651 (C=C) $cm^{-1}$. Its fabms spectrum exhibited a $[MH]^+$ at *m/z* 633, and elemental analysis established a molecular formula of $C_{34}H_{48}O_{11}$. The $^1$H-nmr, $^{13}$C-nmr, and DEPT spectra of **2** (Tables 1 and 2) resembled those of **1**, suggesting that **2** had the same carbon skeleton as **1**. Comparison of the $^1$H- and $^{13}$C-nmr data of **2** with those of **1** showed that the only difference was that the acetoxyl group ($\delta_C$ 169.65) attached to the oxygen at C-15 in **1** was replaced by a tigloyl group [$\delta_H$ 6.40 (1H, q), 1.73 (3H, br s), 1.61 (3H, d); $\delta_C$ 165.90, 128.72, 138.05, 11.71, and 14.48] in **2**. Accordingly, the structure of **2** was assigned as 3,5-diacetate-7,15-ditiglate of the same parent alcohol [**5**] of **1**.

Euphoppin C [**3**], obtained as a colorless gum, gave ir absorption bands at 3476 (OH), 1720 (CO), 1652 (C=C), 1601, and 1497 (Ar) $cm^{-1}$. The fabms spectrum showed a $[MH]^+$ at *m/z* 655, and elemental analysis established a molecular formula of $C_{36}H_{46}O_{11}$. The $^1$H- and $^{13}$C-nmr (DEPT) spectra of **3** (Tables 1 and 2) were very similar to those of **1** and **2** except that a benzoyl group [$\delta_H$

TABLE 1. $^1$H-Nmr Spectral Data of Compounds **1–4**.[a]

| Proton | Compound | | | |
|---|---|---|---|---|
| | **1**[b] | **2**[c] | **3**[c] | **4**[c] |
| 1β ..... | 3.05 dd (8.4, 14.7) | 3.08 dd (8.4, 15.1) | 3.28 dd (8.4, 15.1) | 2.41 dd (8.4, 15.0) |
| 1α ..... | 1.60 dd (3.1, 14.7) | 1.57 m | 1.60 m | 1.69 m |
| 2 ..... | 1.90 m | 1.91 m | 1.93 m | 2.01 m |
| 3 ..... | 4.99 t (3.1) | 4.92 t (3.1) | 4.96 t (3.0) | 5.06 t (3.6) |
| 4 ..... | 2.64 dd (3.1, 10.7) | 2.60 dd (3.1, 10.8) | 2.64 dd (3.0, 10.7) | 3.19 dd (3.4, 10.7) |
| 5 ..... | 5.78 d (10.7) | 5.80 d (10.8) | 5.87 d (10.7) | 5.85 d (10.7) |
| 7 ..... | 5.14 dd (2.2, 11.5) | 4.98 dd (2.5, 11.0) | 5.19 dd (2.5, 10.0) | 5.14 dd (2.5, 11.6) |
| 8β ..... | 1.92 m | 1.80 m | 1.81 m | 1.82 m |
| 8α ..... | 1.34 m | 1.11 m | 1.23 m | 1.26 m |
| 9 ..... | 0.91 m | 0.97 br d (7.0) | 0.98 br d (7.1) | 0.96 m |
| 11 ..... | 0.86 m | 0.87 br d (7.5) | 0.87 br d (7.5) | 0.90 m |
| 12 ..... | 2.44 d (7.0) | 2.45 d (7.5) | 2.50 d (7.5) | 2.46 d (6.8) |
| 14 ..... | 4.15 s | 4.18 s | 4.20 s | 5.60 s |
| 16 ..... | 0.79 d (6.7) | 0.79 d (6.6) | 0.80 d (6.6) | 0.77 d (6.6) |
| 17 ..... | 5.55 s | 5.58 s | 5.66 s | 5.68 s |
| 18 ..... | 1.04 s | 1.03 s | 1.08 s | 1.05 s |
| 19 ..... | 0.97 s | 0.99 s | 1.05 s | 1.01 s |
| 20 ..... | 1.51 s | 1.25 s | 1.31 s | 1.33 s |
| $R^{1d}$ ..... | 2.04 s | 2.04 s | 2.07 s | 2.06 s |
| $R^{2d}$ ..... | 1.79 s | 2.02 s | 2.05 s | 1.84 s |
| $R^{3d}$ ..... | 6.76 q (6.8) | 6.62 q (7.8) | 6.74 q (6.0) | 6.82 q (6.4) |
| | 1.79 br s | 1.71 br s | 1.73 br s | 1.91 br s |
| | 1.77 d (6.8) | 1.56 d (7.8) | 1.58 d (6.0) | 1.79 d (6.4) |
| $R^{4d}$ ..... | 2.03 s | 6.40 q (7.6) | 7.85 br d (7.7) | 7.00 q (7.4) |
| | | 1.73 br s | 7.49 d (7.7) | 1.91 br s |
| | | 1.61 d (7.6) | 7.37 t (7.7) | 1.82 d (7.4) |
| $R^{5d}$ ..... | | | | 2.05 s |

[a]Chemical shifts (ppm), multiplicity, and coupling constants (Hz) in parentheses.
[b]Assignments from $^1$H-$^1$H COSY and $^{13}$C-$^1$H COSY nmr experiments.
[c]Assignments made by comparison with **1**.
[d]See structures of **1–4** for composition of $R^1$–$R^5$.

TABLE 2. $^{13}$C-Nmr Spectral Data of Compounds **1–4**.

| Carbon | Compound | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **1**[a] | | **2**[b] | | **3**[b] | | **4**[b] | |
| | $^{13}$C | DEPT | $^{13}$C | DEPT | $^{13}$C | DEPT | $^{13}$C | DEPT |
| 1 | 44.86 | $CH_2$ | 44.96 | $CH_2$ | 44.96 | $CH_2$ | 44.78 | $CH_2$ |
| 2 | 37.47 | CH | 37.55 | CH | 37.55 | CH | 36.78 | CH |
| 3 | 77.57 | CH | 76.29 | CH | 77.58 | CH | 77.32 | CH |
| 4 | 49.56 | CH | 49.62 | CH | 49.62 | CH | 51.58 | CH |
| 5 | 67.16 | CH | 67.05 | CH | 66.92 | CH | 67.31 | CH |
| 6 | 57.23 | C | 57.60 | C | 57.69 | C | 56.97 | C |
| 7 | 74.12 | CH | 75.52 | CH | 75.52 | CH | 73.96 | CH |
| 8 | 25.77 | $CH_2$ | 25.35 | $CH_2$ | 25.35 | $CH_2$ | 25.62 | $CH_2$ |
| 9 | 23.82 | CH | 24.27 | CH | 24.33 | CH | 24.02 | CH |
| 10 | 19.15 | C | 19.28 | C | 19.40 | C | 19.31 | C |
| 11 | 18.77 | CH | 18.72 | CH | 18.72 | CH | 18.95 | CH |
| 12 | 38.32 | CH | 38.56 | CH | 38.72 | CH | 38.39 | CH |
| 13 | 86.49 | C | 86.36 | C | 86.43 | C | 87.03 | C |
| 14 | 72.22 | CH | 72.22 | CH | 72.36 | CH | 73.20 | CH |
| 15 | 91.05 | C | 91.03 | C | 91.03 | C | 89.80 | C |
| 16 | 14.30 | $CH_3$ | 14.29 | $CH_3$ | 14.48 | $CH_3$ | 14.37 | $CH_3$ |
| 17 | 98.21 | CH | 98.63 | CH | 98.76 | CH | 98.72 | CH |
| 18 | 27.52 | $CH_3$ | 27.42 | $CH_3$ | 27.42 | $CH_3$ | 27.70 | $CH_3$ |
| 19 | 15.85 | $CH_3$ | 15.97 | $CH_3$ | 15.97 | $CH_3$ | 15.92 | $CH_3$ |
| 20 | 25.16 | $CH_3$ | 25.63 | $CH_3$ | 25.69 | $CH_3$ | 25.15 | $CH_3$ |
| $R^1$[c] | 170.74 | CO | 170.55 | CO | 170.62 | CO | 170.71 | CO |
| | 21.03 | $CH_3$ | 21.03 | $CH_3$ | 21.03 | $CH_3$ | 21.05 | $CH_3$ |
| $R^2$[c] | 171.72 | CO | 169.64 | CO | 169.24 | CO | 171.55 | CO |
| | 21.29 | $CH_3$ | 22.93 | $CH_3$ | 22.14 | $CH_3$ | 21.31 | $CH_3$ |
| $R^3$[c] | 165.46 | CO | 165.20 | CO | 165.72 | CO | 165.56 | CO |
| | 137.98 | CH | 137.36 | CH | 139.26 | CH | 137.84 | CH |
| | 128.97 | C | 128.32 | C | 129.88 | C | 128.27 | C |
| | 14.53 | $CH_3$ | 14.28 | $CH_3$ | 14.50 | $CH_3$ | 14.54 | $CH_3$ |
| | 11.92 | $CH_3$ | 11.07 | $CH_3$ | 11.49 | $CH_3$ | 11.98 | $CH_3$ |
| $R^4$[c] | 169.65 | CO | 165.90 | CO | 168.00 | CO | 166.57 | CO |
| | 22.92 | $CH_3$ | 138.05 | CH | 133.00 | CH | 135.58 | CH |
| | | | 128.72 | C | 130.00 | C | 129.17 | C |
| | | | 14.48 | $CH_3$ | 129.88 | 2×CH | 14.54 | $CH_3$ |
| | | | 11.71 | $CH_3$ | 128.14 | 2×CH | 12.30 | $CH_3$ |
| $R^5$[c] | | | | | | | 168.90 | CO |
| | | | | | | | 22.68 | $CH_3$ |

[a]Assignments from $^{13}$C-$^1$H COSY experiments.
[b]Assignments made by comparison with **1**.
[c]See structures of **1–4** for composition of $R^1$–$R^5$.

7.85 (2H, br d), 7.49 (1H, d), 7.37 (2H, t); $\delta_C$ 168.0, 133.00, 130.00, 129.99, 128.14] was attached to C-15 instead of the acetoxyl groups in **1**. Thus, **3** is the 3,5-diacetate-7-tiglate-15-benzoylate of the parent alcohol **5**.

Euphoppin D [**4**] was obtained as a colorless gum. The fabms spectrum of **4** gave a $[MH]^+$ at *m/z* 675, and elemental analysis gave a molecular formula of $C_{36}H_{50}O_{12}$. Comparison of the $^1$H-nmr spectra of **4** and **2** revealed the shift of a signal at δ 4.18 (1H, s, H-14) in **2** downfield to δ 5.60 (1H, s) in **4**, while the comparison of the $^{13}$C-nmr spectrum of **2** with that of **4** indicated that the C-14 signal of **2** was shifted upfield from δ 73.20 to δ 72.22 and the C-15 resonance shifted downfield from δ 89.80 to δ 91.03 in **4**. These data are consistent with the

TABLE 3. NOESY and COLOC Nmr Spectral Interactions for Compound **1**.[a]

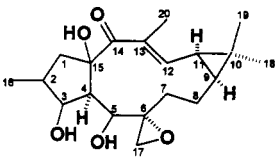
| Position | NOESY (Proton) | COLOC[b] (Carbon) |
|---|---|---|
| 1β | 1α, 14β | |
| 1α | 1β | |
| 2α | 3α, 4α | |
| 3α | 2α, 4α | 15 |
| 4α | 2α, 3α, 17 | (3), (5) |
| 5β | 15-OAc, 12β | 17 |
| 7α | 8α, 9α | |
| 8β | 8α, 19 | |
| 8α | 7α, 8β, 9α | |
| 9α | 7α, 8α, 11α, 18 | |
| 11α | 9α, 18 | |
| 12β | 15-OAc, 5β, 14β, 19 | 5, (6), 10, 14 |
| 14β | 1β, 12β, 20 | 4, (15) |
| 16 | | (2), 3 |
| 17 | 15-OAc, 4α | 13 |
| 18 | 9α, 11α | (10) |
| 19 | 8β, 12β | (10) |
| 20 | 14β | (13) |

[a]The NOESY and COLOC nmr experiments were performed at 400.13/100.16 MHz in $CHCl_3$.

[b]Two-bond correlations are in parentheses.

presence of an acetate group at C-14 instead of the hydroxyl group which is present in **2**. Thus, **4** is the 3,5,14-triacetate-7,15-ditiglate of the parent alcohol **5**.

The polyfunctional parent alcohol [**5**] of euphoppins A [**1–4**] is closely comparable structurally with myrsinol [**6**]. The 13,17-ether bridge in **5** and **6** may be biogenetically derived from 6,17-epoxylathyrol [**7**]. Compound **7** may be considered an oxygenated product of a macrocyclic precursor (lathyrane type) of the hypothetical diterpenes tigliane, ingenane, and daphnane (10,11,16). Therefore, **5** and **6** may represent one of the by-products of biosynthesis of the diterpenes which, after functionalization, appear as the polyfunctional parent alcohols of skin irritant and tumor-promoting diterpene esters occurring in many species of the Euphorbiaceae (17).



7

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Optical rotations were measured in $CHCl_3$ with a Rudolph Research Autopol automatic polarimeter. Ir spectra were recorded on KBr plates as a film using a Nicolet 170-SX ir spectrophotometer. Fabms were run on a VG ZAB-HS mass spectrometer, and $^1$H- and $^{13}$C-nmr spectra were recorded on a Bruker AM 400 spectrometer in $CDCl_3$ with TMS as internal reference.

PLANT MATERIAL.—*Euphorbia aleppica* was collected along the Irbid-Amman highway, Irbid, Jordan, in July 1993. It was identified by Dr. J. Lahham, Biology Department of Yarmouk University, Irbid, Jordan, where a voucher specimen (No. 5601) is deposited.

EXTRACTION AND ISOLATION.—Air-dried and powdered whole plants (850 g) were extracted repeatedly (3×) with petroleum ether (60–90°)-$Et_2O$-MeOH (1:1:1) at room temperature. The combined extracts were evaporated *in vacuo* to give a concentrated solution (65 g). The concentrated extract was absorbed on Si gel and subjected to cc eluting with a gradient of petroleum ether (60–90°)-$Me_2CO$ (50:1→1:5). Three fractions (22 g) were collected, and the second fraction (8 g, 5:1→1:1) was subjected to cc on Si gel and eluted with $CH_2Cl_2$-$Et_2O$ (15:1) to yield three fractions (5 g). Fraction 2 was further chromatographed by Si gel cc with petroleum ether-EtOAc (1:1–1:2) to give five fractions. Fraction 3 was purified by Si gel cc with petroleum ether-$Me_2CO$ (5:1) to afford **4** (9 mg); fraction 4 was purified by Si gel cc with petroleum ether-EtOAc (1:1) to give **3** (6 mg) and **2** (7 mg), and fraction 5 was purified by Si gel with petroleum ether-$Me_2CO$ (1:1) to afford **1** (45 mg).

*Euphoppin A* [**1**].—Obtained as a colorless gum; $[\alpha]^{14}D$ −29.0° (*c*=0.74, $CHCl_3$); ir (KBr) ν max 3646 (OH), 3058–2874 (CH, aliphatic), 1740 (C=O, ester), 1651 (C=C), 1457, 1371, 1226, 1121, 1073, 755 $cm^{-1}$; fabms *m/z* $[MH]^+$ 593 (1), 575 (8), 515 (2), 475 (2), 455 (2), 415 (3), 395 (5), 355 (6), 295 (6), 267 (10), 239 (8), 225 (7), 154 (30), 136 (25), 83 (65), 43 (100); $^1$H-nmr data, see Table 1; $^{13}$C-nmr data, see Table 2; *anal.*, calcd for $C_{31}H_{44}O_{11}$, C 62.82, H 7.48, found C 62.80, H 7.50.

*Euphoppin B* [**2**].—Obtained as a colorless gum; $[\alpha]^{14}D$ −11.5° (*c*=0.80, $CHCl_3$); ir (KBr) ν max 3460 (OH), 3010–2873 (CH, aliphatic), 1720 (C=O, ester), 1651 (C=C), 1456, 1374, 1267, 1132, 1073, 755 $cm^{-1}$; fabms *m/z* $[MH]^+$ 633 (2), 615 (3), 555 (2), 515 (2), 455 (3), 415 (2), 355 (6), 295 (28), 267 (35), 239 (20), 225 (20), 197 (30), 175 (38), 133 (35), 83 (100), 43 (100); $^1$H-nmr data, see Table 1; $^{13}$C-nmr data, see Table 2; *anal.*, calcd for $C_{34}H_{48}O_{11}$, C 64.54, H 7.65, found C 64.51, H 7.65.

*Euphoppin C* [**3**].—Obtained as a colorless gum; $[\alpha]^{14}D$ −7.0° (*c*=0.81, $CHCl_3$); ir (KBr) ν max 3476, 3010, 2936, 2873, 1719, 1652, 1601, 1497, 1456, 1375, 1268, 1131, 1074, 755 $cm^{-1}$; fabms *m/z* $[MH]^+$ 655 (2), 637 (3), 595 (2), 577 (2), 537 (3), 533 (2), 477 (1.5), 473 (3), 417 (3), 373 (4), 313 (10), 267 (35), 239 (20), 225 (25), 175 (40), 105 (100), 83 (100), 43 (100); $^1$H-nmr data, see Table 1; $^{13}$C-nmr data, see Table 2; *anal.*, calcd for $C_{36}H_{46}O_{11}$, C 66.04, H 7.08, found C 66.01, H 7.07.

*Euphoppin D* [**4**].—Obtained as a colorless gum; $[\alpha]^{18}D$ −5.7° (*c*=0.50, $CHCl_3$); ir (KBr) ν max 3461, 3009, 2936, 2874, 1720, 1651, 1456, 1374, 1267, 1133, 1075, 755 $cm^{-1}$; fabms *m/z* $[MH]^+$ 675 (1), 657 (7), 597 (3), 557 (3), 515 (8), 455 (6), 415 (6), 355 (12), 315 (15), 295 (14), 267 (20), 225 (15), 175 (20), 83 (100), 57 (100), 43 (100); $^1$H-nmr data, see Table 1; $^{13}$C-nmr data, see Table 2; *anal.*, calcd for $C_{36}H_{50}O_{12}$, C 64.08, H 7.47, found C 64.11, H 7.48.

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of the People's Republic of China and the Doctoral Program of the State Education Commission of the People's Republic of China.

## LITERATURE CITED

1. F.J. Evans and S.E Taylor, *Prog. Chem. Org. Nat. Prod.*, **44**, 1 (1983).
2. E.H. Seip and E. Hecker, *Phytochemistry*, **23**, 1689 (1984).
3. E. Hecker, *Pure Appl. Chem.*, **49**, 1423 (1977).
4. F.J. Evans and C.J. Soper, *Lloydia*, **41**, 193 (1978).
5. Z.J. Jia, Y.L. Ding, Q.G. Wang, and Y.T. Liu, *Phytochemistry*, **29**, 2343 (1990).
6. Z.J. Jia and Y.L. Ding, *Planta Med.*, **57**, 569 (1991).
7. J.G. Shi, Z.J. Jia, and L. Yang, *Phytochemistry*, **32**, 208 (1993).
8. J.G. Shi, Z.J. Jia, and L. Yang, *Planta Med.*, **60**, 501 (1994).
9. Z.J. Jia, J.G. Shi, and L. Yang, *J. Nat. Prod.*, **57**, 811 (1994).
10. M. Rentzea, E. Hecker, and H. Lotter, *Tetrahedron Lett.*, **23**, 1781 (1982).
11. M. Rentzea and E. Hecker, *Tetrahedron Lett.*, **23**, 1785 (1982).
12. O.F. Christopher, D.C. Joseph, and S.R. Davids, *J. Nat. Prod.*, **52**, 179 (1989).
13. D. Uemura, C. Katayama, E. Uno, K. Sasaki, Y. Hirata, Y.P. Chen, and H.Y. Hsu, *Tetrahedron Lett.*, **21**, 1703 (1975).
14. G.D. Manners and R.Y. Wong, *J. Chem. Soc., Perkin Trans. I*, 2075 (1985).
15. U. Daisuke, N. Kazunori, and H. Yoshimasa, *Tetrahedron Lett.*, 4593 (1976).
16. W. Adolf and E. Hecker, *Isr. J. Chem.*, **16**, 75 (1977).
17. D.G. Wu, B. Sorg, and E. Hecker, *J. Nat. Prod.*, **58**, 480 (1995).

*Received 6 February 1995*