# New Terpenoids from *Maytenus blepharodes*

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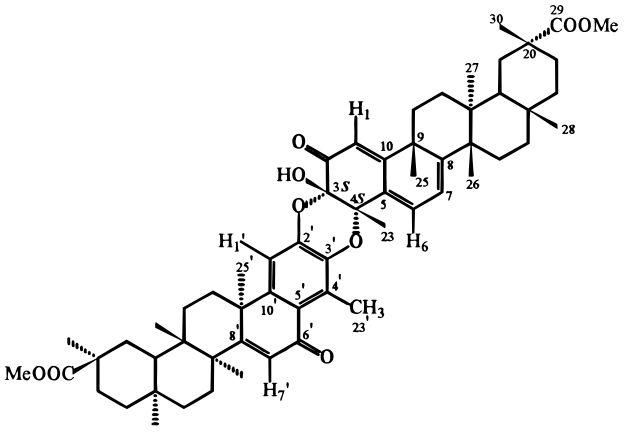
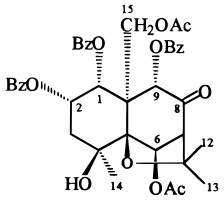
Three new terpenoids, xuxuarine Eα (**1**), a triterpene dimer based on two pristimerin units, and two sesquiterpenoids with a dihydro-*β*-agarofuran skeleton (**2** and **3**) were isolated from *Maytenus blepharodes*. Their structures were elucidated on the basis of spectral analysis, including homonuclear and heteronuclear correlation NMR experiments (COSY, ROESY, HMQC, and HMBC). The absolute configurations of **1** and **2** were determined by CD studies.

As part of our studies on medicinal plants of the family Celastraceae, which are widely used as folk medicines in South[1−3] and Central America,[4,5] we have reported previously triterpene dimers,[6,7] based on nortriterpene methylene quinones and phenols, and a large number of dihydro-*β*-agarofuran sesquiterpenes.[8] Triterpene dimers of this class are composed of one quinoid form and one aromatic form of a nortriterpene derived from pristimerin, tingenone, netzahualcoyene, and/or their congeners, joined by two ether linkages formed between the two A rings[9−11] or between the A and B rings.[12] On the other hand, the sesquiterpene esters, based on the dihydro-*β*-agarofuran [5,11-epoxy-5*β*,10α-eudesman-4(14)-ene] skeleton, have attracted a great deal of interest on account of their antitumor-promotion,[13] reversal of multidrug-resistance,[14] insecticidal,[15] and insect-antifeedant[16] activities. Recently, anti-HIV sesquiterpenes of this type with a new ester linkage have been reported.[17]

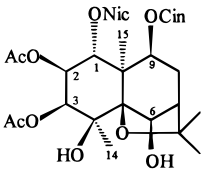
In a previous paper on constituents of *Maytenus blepharodes* Lundell,[18] a species that grows in Panama, we reported two new phenolic triterpenes, blepharodol and 7α-hydroxyblepharodol, together with other known compounds.[19] In an investigation on the remaining fractions of *M. blepharodes*, in addition to the known triterpene dimers scutidin αA; 7,8-dihydroscutidin αB; scutionin αA; 7,8-dihydroscutionin αA; 7,8-dihydroscutionin αB; 7,8-dihydroscutionin *β*B;[7] cangorosin A; 6′,7′-dihydroisocangorosin A;[12] and xuxuarine E*β*,[10] we have isolated a new triterpene dimer (**1**) and two new dihydro-*β*-agarofuran sesquiterpenes (**2** and **3**). Their structures were determined on the basis of spectroscopic data, including $^1$H−$^{13}$C heteronuclear correlation (HMQC), long-range correlation with inverse detection (HMBC), and ROESY NMR experiments. Their absolute configurations were determined by means of CD studies.




Xuxuarine Eα (**1**)




**2**




**3**

## Results and Discussion

A crude (*n*-hexanes−$Et_2O$; 1:1) extract of the roots of *M. blepharodes* was repeatedly chromatographed on Sephadex LH-20 and Si gel to afford **1** (3.6 mg, xuxuarine Eα), **2** (2.2 mg), and **3** (3.0 mg).

Compound **1** was isolated as a pale yellow, amorphous solid with $[\alpha]_D$ +352.2° (*c* 0.32, MeOH). Its FABMS gave a $[M + 1]^+$ ion peak at *m*/*z* 943, and the molecular formula was determined to be $C_{60}H_{78}O_9$, based on FABMS and HREIMS analysis and its $^{13}$C NMR spectrum. Its IR spectrum showed absorption bands for hydroxyl (3444 cm$^{-1}$), carbonyl of ester (1731 cm$^{-1}$), and carbonyl (1677 cm$^{-1}$) groups. In its $^1$H NMR spectrum (Table 1) were observed two singlets at *δ* 6.26 and 6.80 assigned to a proton in the α-position, to an α,*β*-unsatured ketone system (H-7′), and to an aromatic hydrogen (H-1′), together with an ABC system of three vinyl protons at *δ* 6.09 d (*J* = 1.2 Hz), 6.24 dd (*J* = 1.2, 5.2 Hz), and 5.95 d (*J* = 5.2 Hz) attributable to H-1, H-6, and H-7, characteristic of a triterpenic quinoid system. Also were observed signals for 11 angular methyl groups, one methyl group on an aromatic ring at *δ* 2.74, and two methoxy groups at *δ* 3.54 and 3.61 as singlets. These data and the analysis of the $^{13}$C NMR spectrum suggested that **1** was a triterpene dimer

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**Table 1.** $^1$H, $^{13}$C, and HMBC NMR Data for Xuxuarine Eα (**1**)

| | quinoid unit | | | aromatic unit | | |
|---|---|---|---|---|---|---|
| position | $\delta_H$[a] | $\delta_C$[b] | HMBC | $\delta_H$[a] | $\delta_C$[b] | HMBC |
| 1 | 6.09 d (1.2) | 115.1 d | 3, 5, 9 | 6.80 s | 111.3 d | 2′[c], 3′, 5′, 9′ |
| 2 | | 190.2 s | | | 144.5 s | |
| 3 | 5.12 s (OH) | 91.9 s | | | 137.5 s | |
| 4 | | 79.2 s | | | 127.5 s | |
| 5 | | 129.9 s | | | 124.4 s | |
| 6 | 6.24 dd (1.2, 5.2) | 126.7 d | 8, 10 | | 187.8 s | |
| 7 | 5.95 d (5.2) | 116.0 d | 5, 9 | 6.26 s | 126.0 d | 5′, 9′ |
| 8 | | 161.3 s | | | 171.6 s | |
| 9 | | 44.6 s | | | 41.2 s | |
| 10 | | 174.1 s | | | 150.4 s | |
| 11 | | 32.7 t | | | 34.1 t | |
| 12 | | 29.8 t | | | 29.8 t | |
| 13 | | 37.9 s | | | 40.0 s | |
| 14 | | 44.2 s | | | 44.2 s | |
| 15 | | 28.4 t | | | 28.3 t | |
| 16 | | 36.2 t | | | 36.3 t | |
| 17 | | 30.4 s | | | 30.4 s | |
| 18 | | 44.1 d | | | 44.1 d | |
| 19α | 2.42 d | 30.8 t | 29 | 2.42 d | 30.7 t | 29 |
| 20 | (12.5) | 40.3 s | | (12.5) | 40.3 s | |
| 21 | | 29.6 t | | | 29.4 t | |
| 22 | | 34.8 t | | | 34.7 t | |
| 23 | 1.59 s | 22.1 q | 3, 4[c], 5 | 2.74 s | 12.9 q | 3′, 5′ |
| 25 | 1.43 s | 39.4 q | 8, 10 | 1.51 s | 37.6 q | 8′, 10′ |
| 26 | 1.17[d] s | 22.4 q | 8 | 1.26 s | 20.7 q | 8′ |
| 27 | 0.54[e] s | 18.2 q | | 0.55[e] s | 18.6 q | |
| 28 | 1.07 s | 31.5 q | | 1.10 s | 31.5 q | |
| 29 | | 178.7[f] s | | | 178.8[f] s | |
| 30 | 1.16[d] s | 32.6 q | | 1.17[c] s | 32.6 q | |
| OMe | 3.61 s | 51.6 q | 30 | 3.54 s | 51.5 q | 30′ |

[a] δ, $CDCl_3$, *J* values in Hertz. [b] Data are based on DEPT and HMQC experiments. [c] Two-bond coupling enhancement observed. [d–f] Assignments may be interchangeable.

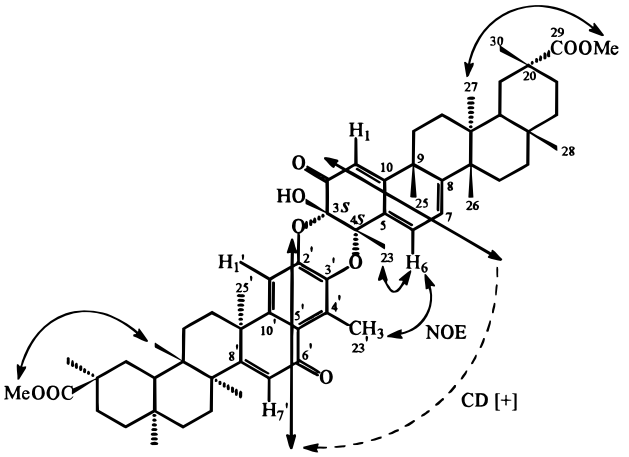


**Figure 1.** NOE effects (↔) and CD exciton coupling (−) for xuxuarine Eα (**1**).

composed of two pristimerin units, one in the quinoid form and other in the aromatic form.[9]

The analysis of its COSY, HMQC, and HMBC spectra enabled the assignment of the signals of the quinoid and aromatic triterpene units, including the signals at C-3 ($\delta_C$ 91.9) and C-4 ($\delta_C$ 79.2) in the 3-hydroxy-4-methyl-3,4-dioxy part of the quinoid unit. The cited values,[7,9] together with the chemical shifts of H-6 ($\delta_H$ 6.24) and C-23 ($\delta_C$ 22.1), suggested a cis orientation about the 3,4-dioxy bond. A ROESY experiment showing a NOE correlation between H-6 and Me-23′ (Figure 1) revealed that the 3,4-dioxy bond in **1** consisted of C-3,C-2′ and C-4,C-3′ linkages.[7]

The absolute configuration of **1** was determined as 3*S*,4*S* by analysis of the CD spectrum, showing a split curve with positive and negative Cotton effects at 349 and 244 nm, respectively (Figure 1). The above data led to the conclusion that compound **1** is an isomer of both xuxuarine E$\beta$[10] and scutidin αA.[7] We propose the name xuxuarine Eα for compound **1**, after the nomenclature initiated by Itokawa et al.[9]

Dimeric compounds with A−A or A−B linkages, implying different stereo- and regio-isomeric relationships, have been reported.[6,7,9–12] These compounds, derived by hypothetical hetero-Diels−Alder reactions, offer the possibility of studying potential enzymatic systems with Diels−Alder-ase activity, as has been put forward by the present authors[20] and by Laschat.[21]

Compound **2** has the molecular formula $C_{40}H_{40}O_{13}$, as shown by HREIMS. Its IR spectrum showed absorption bands for hydroxyl (3683 $cm^{-1}$) and carboxyl groups (1746, 1738, and 1731 $cm^{-1}$). The mass spectrum exhibited peaks consistent with losses of benzoic acid (*m*/*z* 606 [M − $PhCO_2H]^+$) and acetic acid (*m*/*z* 668 [M − HOAc]$^+$) units. Moreover, the $^1$H and $^{13}$C NMR spectra (Experimental Section) of **2** suggested the presence of three benzoate groups [$\delta_H$ 6.89−8.09 (15 H, m); $\delta_C$ 127.8−133.6 (18 × $C_6H_5$−), 165.0 (2 × −COO$^-$), and 165.5 (−COO$^-$)] and two acetate groups [$\delta_H$ 2.13 and 2.18 (each 3H, s); $\delta_C$ 20.6 and 21.3 (2 × Me), 169.3 and 170.4 (2 × −COO$^-$)]. In addition, the $^1$H NMR spectrum (Table 2) contained signals assignable to protons on carbon atoms carrying four secondary ester groups at δ 5.64 dd (1H, *J* = 3.3 Hz, 3.5 Hz, H-2), 6.05 d (1H, *J* = 3.5 Hz, H-1), 6.08 s (1H, H-9), and 6.73 s (1H, H-6) and one primary ester group at δ 5.10 and 5.19 $d_{AB}$ (2H, *J* = 12.9 Hz, H-15). A tertiary methyl group at δ 1.64 s (3H, Me-14) attached to a carbon at δ 69.7 bearing a hydroxyl group; two angular methyl groups at δ 1.69 and 1.72 (each 3H, H-12 and H-13) in the $^1$H NMR spectrum; four quaternary carbons at δ 69.7, 93.3, 52.8, and 85.3; and a carbonyl carbon at δ 197.0 in the $^{13}$C NMR spectrum were also observed. All these data indicated that **2** is a polyester sesquiterpene with a pentasubstituted dihydro-β-agarofuran skeleton.[22]

A careful analysis of the $^1$H−$^1$H COSY NMR spectrum led to the assignment of the five ester-group geminal protons at C-1, C-2, C-6, C-9, and C-15. A ROESY experiment (Figure 2), showing NOE effects between H-1, H-2 and H-9, H-$15_{ab}$, H-6, and Me-14 and between Me-12 and H-9, enabled the relative position of the ester groups to be determined. The regiosubstitution characteristics were further determined by an HMBC experiment (Table 2), showing three-bond coupling between the carbonyl signals of the acetate groups at $\delta_C$ 169.3 and 170.4 and the signals at $\delta_H$ 6.73 (H-6) and $\delta_H$ 5.10−5.19 (H-15), respectively, while the carbonyl signals of the benzoate groups at $\delta_C$ 165.0 (× 2) and 165.5, were correlated with the signals at $\delta_H$ 5.64 (H-2), 6.05 (H-1), and 6.08 (H-9), respectively.

The absolute configuration of **2** was resolved by the dibenzoate chirality method, an extension of the circular dichroism exciton chirality method.[23] The CD spectrum of **2** showed a curve with a positive Cotton effect at 233 nm ($\Delta\epsilon$ = + 26.8) due to the couplings of the chromophoric benzoate at C-9α with the same group at C-1α and C-2α, as the 1,9 pairwise interaction was almost coplanar[24] (Figure 2). Therefore, **2** was identified as (1*R*,2*S*,4*S*,-5*S*,6*R*,7*R*,9*S*,10*S*)-6,15-diacetoxy-1,2,9-tribenzoyloxy-4-hydroxy-8-oxo-dihydro-β-agarofuran.

Compound **3** was assigned the molecular formula $C_{34}H_{39}O_{10}N$, with MS fragments at *m*/*z* 580 [M + H − $CH_2$=CO]$^+$, 477 [580 − $C_6H_5CH$=CH]$^+$, 131 [$C_6H_5CH$=CH−CO]$^+$, 106 [$C_5H_4NCO$]$^+$, and 78 [$C_5H_4N$]$^+$, suggesting

**Table 2.** $^1$H, $^{13}$C NMR and HMBC Data for Compounds **2** and **3**

| | **2** | | | **3** | | |
|---|---|---|---|---|---|---|
| position | $\delta_H$[a] | $\delta_C$[b] | HMBC ($^{13}$C) | $\delta_H$[a] | $\delta_C$[b] | HMBC ($^{13}$C) |
| 1 | 6.05 d (3.5) | 74.3 d | 10[c], 15 | 6.63 d (11.1) | 68.3 d | 15 |
| 2 | 5.64 dd (3.3, 3.5) | 69.7 d | | 5.58 dd (11.1, 3.1) | 68.8 d | 1[c], $CH_3COO^-$ |
| 3 | 2.35 d (3.3) | 42.1 t | 4[c], 14 | 5.41 t (3.3) | 74.9 d | 2[c], 5, $CH_3COO^-$ |
| 4 | | 69.7 s | | 2.80 m | 39.3 d | 2, 5[c], 10, 14[c] |
| 5 | | 93.3 s | | | 88.5 s | |
| 6 | 6.73 s | 74.4 d | 5[c], 11, $CH_3COO^-$ | 5.38 s | 79.9 d | 5[c], 10, 11 |
| 7 | 3.07 s | 64.9 d | 8[c], 5, 9 | 2.22 m | 47.9 d | 6[c], 9 |
| 8 | | 197.0 s | | | 29.7 t | |
| 9 | 6.08 s | 79.6 d | 8[c], 10[c], 1, 15, $C_6H_5COO^-$ | 4.79 d (6.4) | 72.8 d | 5, 7, 15 $C_6H_5CH{=}CHCOO^-$ |
| 10 | | 52.8 s | | | 52.6 s | |
| 11 | | 85.3 s | | | 83.4 s | |
| 12 | 1.69 s | 25.4 q | 7, 11[c], 13 | 1.22 s | 26.1 q | 7, 11[c], 13 |
| 13 | 1.72 s | 29.3 q | 7, 11[c], 12 | 1.41 s | 30.5 q | 7, 11[c], 12 |
| 14 | 1.64 s | 24.6 q | 3, 4[c], 5 | 1.28 d (7.7) | 16.1 q | 3, 4[c], 5 |
| 15 | 5.10, 5.19 $d_{ab}$ (12.9) | 61.8 t | 5, $CH_3COO^-$ 9, 10[c] | 1.58 s | 19.7 q | 1, 5, 9, 10[c] |

[a] $\delta$, $CDCl_3$, $J$ values in Hertz. [b] Data are based on DEPT and HMQC experiments. [c] Two-bond coupling enhancement observed.

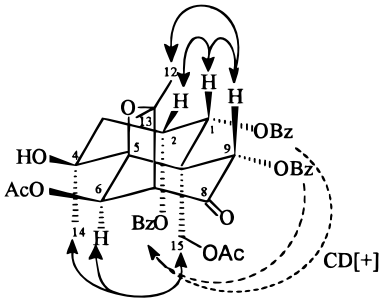


**Figure 2.** NOE effects (↔) and CD exciton couplings (- - -) for compound **2**.

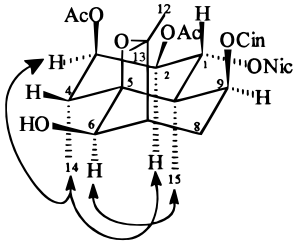


**Figure 3.** NOE effects for compound **3**.

the presence of acetate, cinnamoyl, and nicotinoyl ester groups. Its IR spectrum showed absorption bands for hydroxyl and ester groups. The $^1$H NMR spectrum (Experimental Section) also indicated the presence of two acetate methyl groups as singlets at $\delta$ 1.81 and 2.10, one cinnamoyl group with five aromatic protons between $\delta$ 7.29−7.59 and the two olefinic protons at $\delta$ 6.40 ($J$ = 16.0 Hz) and 7.50 ($J$ = 16.0 Hz), and one nicotinoyl group at $\delta$ 9.55 br s, 8.86 br d ($J$ = 5.0 Hz), 8.57 br d ($J$ = 7.9 Hz), and 7.75 m. The $^1$H NMR spectrum (Table 2) also contained signals assignable to protons on carbon atoms carrying four secondary ester groups at $\delta$ 6.63 d (1H, $J$ = 11.1 Hz, H-1), 5.58 dd (1H, $J$ = 11.1 Hz, 3.1 Hz, H-2), 5.41 t (1H, $J$ = 3.3 Hz, H-3), and 4.79 d (1H, $J$ = 6.4 Hz, H-9); one secondary hydroxyl group at $\delta$ 5.38 s (1H, H-6); and four methyl groups at $\delta$ 1.22 s (Me-12), 1.28 d ($J$ = 7.7 Hz, Me-14), 1.41 s (Me-13), and 1.58 s (Me-15), which were confirmed by the $^{13}$C NMR spectrum (Table 2). These data suggested the presence of a 1,2,3,6,9-pentasubstitued dihydro-$\beta$-agarofuran skeleton.[24]

An HMBC experiment (Table 2) enabled the regiosubstitution patterns to be established with acetate groups on C-2 and C-3, a nicotinate unit at C-1, a cinnamate unit at C-9, and the hydroxy group at C-6. The relative stereochemistry of **3** was resolved by analysis of the ROESY experiment (Figure 3), showing significant effects among H-2, H-3, and Me-14 and among H-9, H-6, and Me-15. Therefore, the structure of **3** was established as 9$\beta$-cinnamoyloxy-2$\beta$,3$\beta$-diacetoxy-6$\beta$-hydroxy-1$\alpha$-nicotinoyloxy-dihydro-$\beta$-agarofuran.

Compounds **2** and **3** have the basic polyhydroxylated skeletons of 3,13-dideoxyevoninol[25] and 4-deoxymagellanol,[24] respectively.

## Experimental Section

**General Experimental Procedures.** Optical rotations were measured on a Perkin−Elmer 241 automatic polarimeter, and the $[\alpha]_D$ are given in $10^{-1}$ deg cm$^2$ g$^{-1}$. CD spectra were run on a JASCO J-600 spectropolarimeter. IR spectra were recorded in $CHCl_3$ on a Bruker IFS 55 spectrophotometer, and UV spectra were collected in absolute EtOH on a JASCO V-560. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer at 400 and 100 MHz, respectively. EIMS and HREIMS were recorded on a Micromass Autospec spectrometer, and FABMS was recorded on a VG Autospec mass spectrometer. TLC 1500/LS 25 Schleicher and Schuell foils were used for TLC, while Si gel (0.2−0.63 mm) and Sephadex LH-20 were used for column chromatography.

**Plant Material.** *M. blepharodes* was collected at Volcán Varu, Chirique, Panamá, in August 1991, and a voucher specimen is on file in the Department of Medicinal Chemistry and Pharmacognosy, University of Panamá. The root bark of the plant (500 g) was extracted with *n*-hexanes−$Et_2O$ (1:1) (4 L) in a Soxhlet apparatus. The extract (10 g) was chromatographed on Sephadex LH-20, using *n*-hexane−$CHCl_3$−MeOH (2:1:1) as eluent to afford 17 fractions. Fraction 4 (910 mg), after chromatography over Si gel (*n*-hexanes−EtOAc mixtures of increasing polarity) and preparative HPTLC (HPTLC−Platten-SIL 20 $UV_{254}$) (*n*-hexane−$CHCl_3$−acetone, 6:3:1), gave rise to compound **1** (3.6 mg), not previously described, in addition to the six known compounds: scutidin $\alpha$A (65.0 mg); 7,8-dihydroscutidin $\alpha$B (97.0 mg); scutionin $\alpha$A (30.0 mg); 7,8-dihydroscutionin $\alpha$A (24.2 mg); 7,8-dihydroscutionin $\alpha$B (15.5 mg); 7,8-dihydroscutionin $\beta$B (7.0 mg); cangorosin A (6.8 mg);

6′,7′-dihydroisocangorosin A (13.7 mg); and xuxuarine E$\beta$ (2.5 mg). Compounds **2** (2.2 mg) and **3** (3.0 mg) were obtained from fraction 8 (990 mg) through a process similar to the one described above, using as eluent in the preparative HPTLC *n*-hexanes−EtOAc−acetone (5:4:1). The known compounds were identified by spectroscopic methods and by comparison with authentic samples or reported data.[7,10,12]

**Xuxuarine Eα (1):** obtained as a pale yellow, amorphous solid; $[\alpha]^{25}_D$ +352.2° (*c* 0.32, $CHCl_3$); CD $\lambda_{max}$ (MeOH) nm 349 ($\Delta\epsilon = +13.5$), 295 ($\Delta\epsilon = +9.5$), 244 ($\Delta\epsilon = -18.9$); UV (EtOH) $\lambda_{max}$ (log $\epsilon$) 383 (2.84), 289 (3.66), 254 (3.93) nm; IR $\nu_{max}$ 3444, 2925, 2870, 1731, 1677, 1650, 1581, 1463, 1377, 1308, 1201, 1144, 1100, 871, 802, 755 $cm^{-1}$; $^1H$ and $^{13}C$ NMR data, see Table 1; HREIMS *m*/*z* $[M_{1/2} + H]^+$ 480.2880 (calcd for $C_{30}H_{40}O_5$, 480.2875), $[M_{1/2} + H]^+$ 464.2972 (calcd for $C_{30}H_{40}O_4$, 464.2926); FABMS *m*/*z* 943 $[M + 1]^+$ (100), 942 $[M]^+$ (5), 480 (51), 464 (86).

**(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6,15-Diacetoxy-1,2,9-tribenzoyloxy-4-hydroxy-8-oxo-dihydro-*β*-agarofuran (2):** obtained as a colorless solid; $[\alpha]^{25}_D$ +47.6° (*c* 0.46, $CHCl_3$); CD $\lambda_{max}$ (MeOH) nm 233 ($\Delta\epsilon = +26.8$), 220 ($\Delta\epsilon = -2.9$); UV (EtOH) $\lambda_{max}$ (log $\epsilon$) 229 nm (4.54); IR $\nu_{max}$ 3683, 3025, 2500, 1746, 1738, 1731, 1209, 1096, 709 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 2.18 (3H, s, Ac-6), 2.13 (3H, s, Ac-15), 2.35 (1H, d, $J$ = 3.3 Hz, OH), OBz [8.09 (2H, m), 7.61 (6H, m), 7.34 (2H, m), 7.13 (3H, m), 6.89 (2H, m)], for other signals, see Table 2; $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ OAc [20.6, 21.3 (2 × $-CH_3$), 170.4 ($-CO_2$), 169.3 ($-CO_2^-$)], OBz [127.8, 128.0, 128.8, 129.3, 129.4, 129.6 (each 2 × CH), 132.9, 133.0 and 133.6 (each CH), 128.2, 128.6, 129.2 (each quaternary carbons), 165.0 (2 × $-CO_2^-$) 165.5 ($-CO_2^-$)], for other signals, see Table 2; EIMS *m*/*z* 728 $[M]^+$ (0.1), 712 (1), 668 (1), 653 (1), 625 (1), 610 (1), 608 (11), 607 (1), 606 (2), 605 (4), 565 (1), 563 (5), 441 (1), 381 (1), 324 (2), 248 (2), 217 (18), 165 (6), 122 (7), 105 (100); HREIMS *m*/*z* $[M - 122]^+$ 606.21148 (calcd for $C_{33}H_{34}O_{11}$, 606.21011).

**9*β*-Cinnamoyloxy-2*β*,3*β*-diacetoxy-6*β*-hydroxy-1α-nicotinoyloxydihidro-*β*-agarofuran (3):** obtained as a colorless solid; $[\alpha]^{25}_D$ +10.0° (*c* 0.13, $CHCl_3$); UV (EtOH) $\lambda_{max}$ (log $\epsilon$) 273 (3.75), 223 (4.03), 218 (4.03) nm; IR $\nu_{max}$ 3444, 2924, 2854, 1731, 1635, 1592, 1454, 1367, 801, 711 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ OAc [1.81 (3H, s, Ac-2), 2.10 (3H, s, Ac-3)], 2.34 (1H, m, H-8), OCin [7.29−7.59 (5H, m), 7.50 (1H, d, $J$ = 16.0 Hz), 6.40 (1H, d, $J$ = 16.0 Hz)], ONic [9.55 (1H, br s), 8.86 (1H, br d, $J$ = 5.0 Hz), 8.57 (1H, br d, $J$ = 7.9 Hz), 7.75 (1H, m)], for other signals, see Table 2; $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ OAc [20.7, 21.4 (2 × $CH_3$), 170.0, 170.6 (2 × $-CO_2^-$)], OCin [118.1 ($-CH{=}CHCOO^-$), 145.3 ($-CH{=}CHCOO^-$), 128.3 (2 × CH), 128.8 (2 × CH) 129.3 (CH), 134.6, 165.9 ($-CO_2^-$)]; ONic [123.2, 137.5, 151.8, 153.4 (each CH), 126.8, 165.0 ($-CO_2^-$)], for other signals, see Table 2; EIMS *m*/*z* 622 $[M + 1]^+$ (1), 590 (1), 580 (6), 519 (1), 478 (2), 477 (4), 316 (4), 291 (1), 281 (1), 280 (2), 278 (2), 257 (3), 255 (3), 243 (2), 230 (3), 229 (3), 215 (2), 194 (4), 179 (5), 173 (5), 151 (6), 149 (6), 131 (31), 125 (16), 124 (12), 123 (13), 106 (13), 105 (58), 103 (7), 78 (5).

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