Two New Sesquiterpene Polyol Esters from *Celastrus angulatus*

by **Shao-Peng Wei**[a]), **Wen-Jun Wu***[a]), **Zhi-Qin Ji**[a]), **Ji-Wen Zhang**[b]), **Yong-Ze Guo**[c]), and **Jian Xue**[d])

[a]) Institute of Pesticides, Northwest A&F University, Yangling, Shaanxi 712100, P. R. China (phone: +86-29-87092191; fax: +86-29-87093987; e-mail: wuwenjun@nwsuaf.edu.cn)

[b]) College of Sciences, Northwest A&F University, Yangling, Shaanxi 712100, P. R. China

[c]) Central Laboratory of Tianjin Academy of Agricultural Sciences, Tianjin 300381, P. R. China

[d]) Institute of Medicinal Plant Development in Chinese Academy of Medical Sciences, Beijing 100193, P. R. China

Two novel sesquiterpene polyol esters with a dihydro-β-agarofuran (=(3*R*,5a*S*,9*R*,9a*S*)-octahydro-2,2,5a,9-tetramethyl-2*H*-3,9a-methano-1-benzoxepin) skeleton, (1α,2α,4β,8α,9α)-1,2,8,12-tetrakis(acetyloxy)-9-(furoyloxy)-4-hydroxydihydro-β-agarofuran (**1**) and (1α,2α,6β,8α,9α)-1,2,6,8,12-pentakis(acetyloxy)-9-(benzoyloxy)dihydro-β-agarofuran (**2**), and the three known compounds (1α,2α,4β,6β,8α,9β)-1,2,6-tris(acetyloxy)-9-(benzoyloxy)-4-hydroxy-8,12-bis(isobutyryloxy)dihydro-β-agarofuran (**3**), (1α,2α,4β,6β,8α,9β)-1,2,6,8-tetrakis(acetyloxy)-9-(furoyloxy)-4-hydroxy-12-isobutyryloxy)dihydro-β-agarofuran (**4**), and (1α,2α,4β,6β,8α,9β)-1,2,6-tris(acetyloxy)-9-(benzoyloxy)-4-hydroxy-8-(isobutyryloxy)-12-[(2-methylbutanoyl)oxy]dihydro-β-agarofuran (**5**) were isolated from the root bark of *Celastrus angulatus*. Their chemical structures were elucidated by analyses of their MS and NMR data.

Introduction. – Plant-derived products with insecticidal activities are a valuable source for new lead compounds. In our program for screening new bioactive natural products from the extract of the root bark of *Celastrus angulatus* (Celastraceae), various insecticidal dihydro-β-agarofuran sesquiterpene polyol esters and alkaloids have been isolated [1–4] (dihydro-β-agarofuran = (3*R*,5a*S*,9*R*,9a*S*)-octahydro-2,2,5a,9-tetramethyl-2*H*-3,9a-methano-1-benzoxepin).

The sesquiterpene polyol esters with dihydro-β-agarofuran skeleton have attracted considerable attention from synthetic organic chemists and pharmacologists due to their complex structures and wide range of biological properties, including immunosuppressive [5][6], cytotoxic [7], anti-HIV [8], reversing multi-drug-resistance (MDR) phenotype [9–12], antitumor [13][14], and insect narcotic and insecticidal activities [1–4][15][16]. On the basis of their biological and structural properties, these sesquiterpenes have been selected as 'privileged structures' [10][17][18].

Previous studies showed that the activity of compounds with the same skeleton varied with the nature of the esterifying residues against *Mythimna separate*. We wanted to known how the molecular features (the number and the orientation of the ester group) affect the biological activity. Therefore, the chemical constituents of the root bark of *C. angulatus* were re-investigated to obtain a sufficient number of compounds for a significant correlation of the QSAR (quantitative structure-activity relationship). These studies have led to the isolation of two novel sesquiterpene polyol

esters, **1**[1]) and **2**[1]), and the three known compounds **3**–**5** from the root bark of this plant (*Fig. 1*). In this article, the isolation and structure identification of compounds **1**–**5** are described.

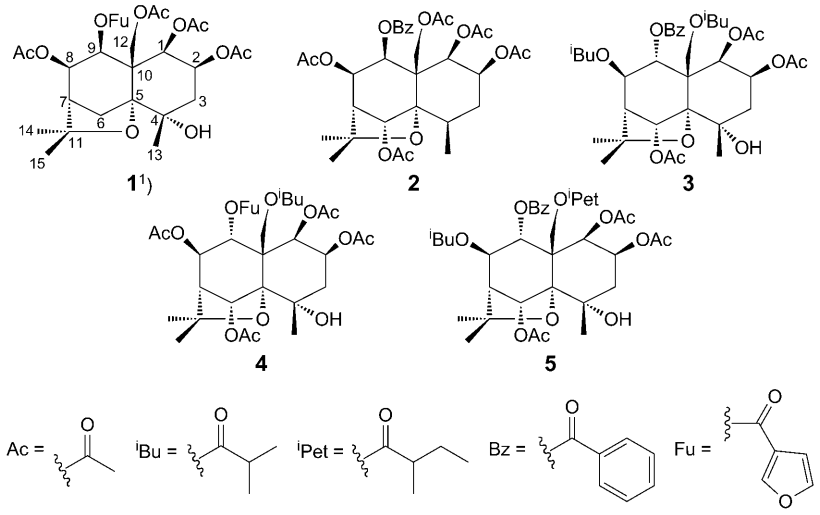

Fig. 1. *Compounds* **1**–**5** *isolated from* Celastrus angulatus

Results and Discussion. – The air-dried root bark of *C. angulatus* was extracted with benzene to obtain the crude extract. The crude extract was re-extracted with MeOH. The MeOH extract was subjected to column chromatography (macroporous resin, then repeatedly silica gel) and reversed-phase HPLC to yield compounds **1**–**5**. Their structures were elucidated on the basis of UV, HR-ESI-MS, and NMR spectroscopic data.

Compound **1** was an amorphous white powder, whose molecular formula $C_{28}H_{36}O_{13}$ was determined by HR-ESI-MS (positive-ion mode) and ^{1}H- and ^{13}C-NMR spectroscopy (*Table*). The IR spectrum revealed characteristic ester absorptions at 1723 cm^{-1} and a free OH absorption at 3493 cm^{-1}. The UV spectrum contained an absorption of an aromatic moiety (UV/VIS: λ_{max} (MeOH) 230 nm). The ESI-MS/MS exhibited peaks attributable to the presence of an acetate (*m*/*z* 543 ($[M+\mathrm{Na}-60]^+$)) and a furoate group *m*/*z* 491 (($[M+\mathrm{Na}-112]^+$)) (*Fig. 2*). This was confirmed by the ^{1}H-NMR spectrum, which also indicated the presence of signals for four AcO groups at δ(H) 1.73, 1.93, 2.11, and 2.26 (4*s*, each 3 H) and three H-atoms in the aromatic region for a furoyl group at δ(H) 8.04 (*d*, *J* = 1.5, 1 H), 7.44 (*s*, 1 H), and 6.74 (*d*, *J* = 1.5, 1 H). Based on previously published data [2][3], the ^{1}H,^{1}H-COSY cross-peaks at δ(H) 5.50 (*d*, *J* = 3.5, H–C(1))/5.48–5.50 (*m*, H–C(2)) and δ(H) 5.66 (*dd*, *J* = 3.0, 3.5, H–C(8))/5.51 (*d*, *J* = 3.5, H–C(9)) were assigned to four H-atoms attached to C-atoms bearing secondary ester groups, while the signals at δ(H) 4.67 (*d*, *J* = 12.5, H_α–C(12)) and

[1]) Trivial atom numbering; for systematic names, see *Exper. Part.*

Table. *^{1}H- and ^{13}C-NMR Data* (500 MHz, $CDCl_3$) *of Compounds* **1** *and* **2**[a])[1])

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(1)	5.50 (*d*, *J* = 3.5)	70.2	5.62 (*d*, *J* = 5.0)	70.1
H–C(2)	5.48–5.50 (*m*)	68.8	5.59–5.60 (*m*)	69.1
CH_2(3)	2.15–2.17 (*m*)	31.6	2.46–2.48 (*m*), 1.78–1.79 (*m*)	31.3
C(4) or H–C(4)	–	69.7	2.40–2.42 (*m*)	32.8
C(5)	–	89.3	–	90.4
CH_2(6) or H–C(6)	2.57–2.59 (*m*), 2.32–2.33 (*m*)	40.7	6.74 (*s*)	77.1
H–C(7)	2.60 (*d*, *J* = 3.0)	48.1	2.34 (*d*, *J* = 4.0)	53.2
H–C(8)	5.66 (*dd*, *J* = 3.5, 3.0)	71.3	5.40 (*dd*, *J* = 4.0, 4.0)	74.7
H–C(9)	5.51 (*d*, *J* = 3.5)	67.9	5.55 (*d*, *J* = 4.0)	72.4
C(10)	–	52.2	–	51.4
C(11)	–	83.9	–	81.3
CH_2(12)	4.67 (*d*, *J* = 12.5), 4.50 (*d*, *J* = 12.5)	64.9	5.11 (*d*, *J* = 13.5), 4.86 (*d*, *J* = 13.5)	60.3
Me(13)	1.34 (*s*)	25.1	1.19 (*d*, *J* = 7.5)	16.6
Me(14)	1.63 (*s*)	31.0	1.58 (*s*)	30.4
Me(15)	1.44 (*s*)	25.3	1.44 (*s*)	24.7

[a]) Assignments are based on DEPT and ^{1}H,^{13}C (HSQC and HMBC) experiments.

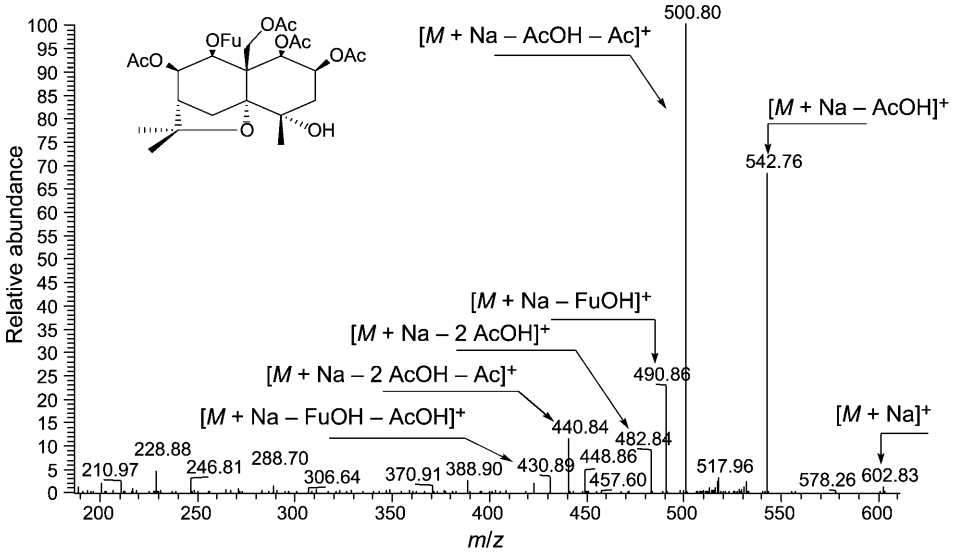

Fig. 2. *ESI-MS/MS of compound* **1**. FuOH = furoic acid.

4.50 (*d*, *J* = 12.5, H_β–C(12)) were assigned to the two H-atoms attached to a C-atom bearing a primary ester group.

The ^{13}C-NMR and DEPT spectra of the parent skeleton of **1** revealed three Me groups at δ(C) 25.1, 25.3, and 31.0, three CH_2 groups at δ(C) 31.6, 40.7, and 64.9, five

CH groups at δ(C) 48.1, 67.9, 68.8, 70.2, and 71.3, and four quaternary C-atoms at δ(C) 52.2, 69.7, 83.9, and 89.3. Their chemical shifts were very similar to those of other known dihydro-β-agarofurans [2][3]. HMBCs of H–C(9) with the CO group at δ(C) 162.1 of the furoate ester, and of H–C(1), H–C(2), H–C(8), and H–C(12) with the CO groups at δ(C) 170.6, 169.9, 169.8, and 169.6 of four acetate esters, respectively, were present. One free OH group was positioned at C(4), as shown by the ^{1}H-NMR data, because the normal value of H–C(6) is generally greater than or near to δ(H) 6.00 when H–C(6) is esterified [2]. The relative configuration of **1** was established on the basis of a NOESY plot: the correlation H–C(1)/H–C(9) indicated the presence of H_{eq}–C(9), and the correlation Me(14)/H–C(8) indicated the presence of H_{eq}–C(8) (*Fig. 3*). Thus, the structure of compound **1** was identified as (1α,2α,4β,8α,9α)-1,2,8,12-tetrakis(acetyloxy)-9-(furoyloxy)-4-hydroxydihydro-β-agarofuran[1]).

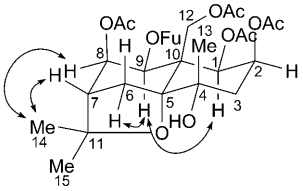

Fig. 3. *Major NOESY correlations of compound* **1**[1])

Compound **2**, an amorphous white powder, had the molecular formula $C_{32}H_{40}O_{13}$ as deduced from the HR-ESI-MS (positive-ion mode) and ^{1}H- and ^{13}C-NMR spectra (*Table*). The IR spectrum revealed characteristic ester absorptions at 1736 cm^{-1}. The UV spectrum contained an absorption of an aromatic moiety (UV/VIS: λ_{max} (MeOH) 240 nm). The ESI-MS/MS contained fragmentation ions suggesting the presence of acetate and benzoate ester groups. This was confirmed by the NMR data, which also indicated the presence of five AcO and one PhCOO ester group in **2**. The ^{13}C-NMR (DEPT) of the parent skeleton suggested that **2** contained a 1,2,6,8,9,12-hexasubstituted dihydro-β-agarofuran skeleton, because there are signals of three Me groups at δ(C) 16.6, 24.7, and 30.4, of two CH_2 groups at δ(C) 31.3 and 60.3, of seven CH groups at δ(C) 32.8, 53.2, 69.1, 70.1, 72.4, 74.7, and 77.1, and of three quaternary C-atoms at δ(C) 51.4, 81.3, and 90.4. HMBCs of H–C(9) with the CO group at δ(C) 164.8 of the benzoate ester, and of H–C(1), H–C(2), H–C(6), H–C(8), and H–C(12) with the CO groups at δ(C) 170.5, 170.0, 169.9, 169.8, and 169.7 of five acetate esters, respectively, were present. The relative configuration of **2** was established on the basis of a NOESY plot: the correlation H–C(1)/H–C(9) indicated the presence of H_{eq}–C(9), and the correlation Me(14)/H–C(8) indicated the presence of H_{eq}–C(8). Thus, the chemical structure of compound **2** was identified as (1α,2α,6β,8α,9α)-1,2,6,8,12-pentakis(acetyloxy)-9-(benzoyloxy)dihydro-β-agarofuran[1]).

Compounds **3**–**5** were three known compounds, *i.e.*, (1α,2α,4β,6β,8α,9β)-1,2,6-tris(acetyloxy)-9-(benzoyloxy)-4-hydroxy-8,12-bis(isobutyryloxy)dihydro-β-agarofuran (**3**), (1α,2α,4β,6β,8α,9β)-1,2,6,8-tetrakis(acetyloxy)-9-(furoyloxy)-4-hydroxy-12-(isobutyryloxy)dihydro-β-agarofuran (**4**), and (1α,2α,6β,8α,9β)-1,2,6-tris(acetyloxy)-9-(benzoyloxy-4-hydroxy-8-(isobutyryloxy)-12-[(2-methylbutanoyl)oxy]dihydro-β-agarofuran (**5**), based on UV, IR, ESI-MS, ^{1}H- and ^{13}C-NMR spectroscopic data [2][4].

This work was supported by the *National Key S&T Research Foundation of China* (2010CB126105), the *National Natural Science Foundation of China* (30871663), the *State Important Sci-Tech Special Projects* (2009ZX09502-027), and the *China Postdoctoral Science Foundation* (Project No. 20100471644).

Experimental Part

General. Solvents were of anal.-reagent (AR) grade unless otherwise mentioned. TLC: *E. Merck 60* F_{254} silica gel plates. Flash column chromatography (FC): C_{18} silica gel (particle size 15 μm; *Fuji Silysia Chemical Ltd.*). HPLC (purification of **1**–**5**): *Shimadzu-6AD* HPLC apparatus; prep. C_{18} column (20 × 250 mm; 10 μm); MeOH/H_2O 7:3 as eluent; UV detector at 230 nm. M.p.: *Yanagimoto* apparatus; uncorrected. ^{1}H-NMR Spectra: *Bruker-Avance-500* spectrometer; $CDCl_3$ as solvent and $SiMe_4$ as internal standard. ESI-MS (positive-ion mode): *Thermo-Finnigan-LCQ-Advantage-MAX* LC/MS mass spectrometer (USA); molecular scan range 100–1000 amu.

Plant Material. The root bark of *C. angulatus* was collected in Qinling Mountain, Taibai County, Shaanxi Province, P. R. China, in October 2006, and authenticated by Prof. *Hua Yi* of the College of Life Sciences, Northwest Agricultural & Forestry University. The voucher specimens (samples No. NWAU2006-A18) were deposited with the College of Life Sciences, Northwest Agricultural & Forestry University.

Extraction and Isolation. The dried and pulverized root bark (3.5 kg) of *C. angulatus* was extracted 3 × with benzene under reflux for 4 h. The extracted material was re-extracted 2 × with MeOH. The re-extracted extracts were concentrated to give a yellow semi-solid residue (500 g). This residue was subjected to CC (*D101* macroporous resin (12.0 × 150 cm), MeOH/H_2O 5:5, 6:4, 7:3, and 8:2): 200 fractions of *ca.* 500 ml each which were combined to 10 fractions (TLC monitoring). Then the fractions were successively subjected to CC (silica gel (200–300 mesh), petroleum ether/acetone/MeOH of increasing polarity) and reversed-phase FC (C_{18}, MeOH/H_2O). In this way, after several CC (silica gel, petroleum ether/acetone or acetone/MeOH), reversed-phase FC (C_{18}, MeOH/H_2O) and pre-HPLC, two new compounds **1** (48 mg) and **2** (467 mg), and the three known compounds **3** (91 mg), **4** (120 mg), and **5** (213 mg) were isolated.

Furan-3-carboxylic Acid rel-*(3*R*,4*S*,5*R*,5a*R*,6*S*,7*R*,9*R*,9a*S*)-4,6,7-Tris(acetyloxy)-5a-[(acetyloxy)methyl]octahydro-9-hydroxy-2,2,9-trimethyl-2*H*-3,9a-methano-1-benzoxepin-5-yl Ester* (**1**): Amorphous white powder. M.p. 165–167°. $[\alpha]_D = -2.0$ ($c = 0.50$, acetone). UV/VIS (MeOH): 230. ^{1}H-NMR ($CDCl_3$): 8.04 (*s*, 1 H (Fu)); 7.44 (*s*, 1 H (Fu)); 6.74 (*d*, $J = 1.5$ (Fu)); 2.26, 2.11, 1.92, 1.73 (4*s*, 4 Ac); 1.63 (*s*, Me(14)); 1.44 (*s*, Me(15)); 1.34 (*s*, Me(13)). ^{13}C-HMR ($CDCl_3$): 170.7 (Me*C*O); 169.9 (Me*C*O); 169.8 (Me*C*O); 169.6 (Me*C*O); 162.1 (CO (Fu)); 148.8 (CH (Fu)); 144.0 (CH (Fu)); 118.5 (C (Fu)); 110.0 (CH (Fu)); 21.5 (*Me*CO); 21.3 (*Me*CO); 21.0 (*Me*CO); 20.5 (*Me*CO). ESI-MS/MS: 603 (1, $[M + Na]^+$), 543 (68, $[M + Na - AcOH]^+$), 501 (100, $[M + Na - AcOH - Ac]^+$), 491 (23, $[M + Na - FuOH]^+$), 483 (10, $[M + Na - 2\ AcOH]^+$), 441 (10, $[M + Na - 2\ AcOH - Ac]^+$), 431 (3, $[M + Na - FuOH - AcOH]^+$). HR-ESI-MS: 598.2489 ($[M + NH_4]^+$, $[C_{28}H_{36}O_{13} + NH_4]^+$; calc. 598.2494).

rel-*(3*R*,4*R*,5*S*,5a*S*,6*R*,7*S*,9*R*,9a*S*,10*R*)-5a-[(Acetyloxy)methyl]octahydro-2,2,9-trimethyl-2*H*-3,9a-methano-1-benzoxepin-4,5,6,7,10-pentol 4,6,7,10-Tetraacetate 5-Benzoate* (**2**): Amorphous white powder. M.p. 148–150°. $[\alpha]_D = +12.0$ ($c = 0.50$, acetone). UV/VIS (MeOH): 240. ^{1}H-NMR ($CDCl_3$): 8.02 (*d*, $J =$ 7.0, 2 arom. H); 7.58 (*t*, $J = 7.5$, 1 arom. H); 7.47 (*t*, $J = 7.5$, 2 arom. H); 2.30, 2.13, 2.08, 2.06, 1.49 (5*s*, 5 Ac); 1.58 (*s*, Me(14)); 1.44 (*s*, Me(15)); 1.19 (*d*, $J = 7.5$, Me(13)). ^{13}C-HMR ($CDCl_3$): 170.5 (Me*C*O); 170.0 (Me*C*O); 169.9 (Me*C*O); 169.8 (Me*C*O); 169.7 (Me*C*O); 164.8 (Ph*C*O); 133.6 (CH (Bz)); 129.7 (2 CH (Bz)); 129.3 (C (Bz)); 128.8 (2 CH (Bz)); 21.6 (*Me*CO); 21.5 (*Me*CO); 21.4 (*Me*CO); 21.1 (*Me*CO); 20.4 (*Me*CO). ESI-MS/MS: 655 (6, $[M + Na]^+$), 595 (100, $[M + Na - AcOH]^+$), 553 (52, $[M + Na - AcOH - Ac]^+$), 533 (27, $[M + Na - BzOH]^+$), 491 (9, $[M + Na - BzOH - Ac]^+$), 473 (7, $[M + Na - BzOH - AcOH]^+$). HR-ESI-MS: 650.2803 ($[M + NH_4]^+$, $[C_{32}H_{40}O_{13} + NH_4]^+$; calc. 650.2807).

2-Methylpropanoic Acid rel-*[(3*R*,4*R*,5*R*,5a*S*,6*R*,7*S*,9*S*,9a*S*,10*R*)-6,7,10-Tris(acetyloxy)-5-(benzoyloxy)octahydro-9-hydroxy-2,2,9-trimethyl-4-(2-methyl-1-oxopropoxy)-5a*H*-3,9a-methano-1-benzoxepin-5a-yl]methyl Ester* (**3**): Amorphous white powder. M.p. 92–95°. UV/VIS (MeOH): 241. ^{1}H-NMR ($CDCl_3$): 8.01 *d*, $J = 7.2$, 2 arom. H); 7.60 (*t*, $J = 7.5$, 1 arom. H); 7.45 (*t*, $J = 7.5$, 2 arom. H); 2.64–2.66 (*m*,

1 Me_2CHCO); 2.67–2.69 (*m*, Me_2CHCO); 2.11, 2.08, 1.46 (3*s*, 3 AcO); 1.69 (*s*, Me(14)); 1.59 (*s*, Me(15)); 1.55 (*s*, Me(13)); 1.27 (*d*, *J* = 7.5, 1 Me_2CHCO); 1.25 (*d*, *J* = 7.5, 1 Me_2CHCO). ^{13}C-HMR ($CDCl_3$): 178.0 (Me_2CHCO); 176.7 (Me_2CHCO); 172.1 (MeCO); 171.5 (MeCO); 171.3 (MeCO); 165.8 (PhCO (Bz)); 134.9 (CH (Bz)); 131.1 (CH (Bz)); 131.2 (CH (Bz)); 129.8 (CH (Bz)); 129.6 (CH (Bz)); 129.4 (C (Bz)); 35.3 (Me_2CHCO); 35.2 (Me_2CHCO); 21.4 (MeCO); 21.1 (MeCO); 20.7 (MeCO); 19.5 (Me_2CHCO); 19.4 (Me_2CHCO); 19.3 (Me_2CHCO); 19.2 (Me_2CHCO). ESI-MS/MS: 727 (9, $[M+Na]^+$, $[C_{36}H_{48}O_{11}+Na]^+$), 667 (96, $[M+Na-AcOH]^+$), 639 (100, $[M+Na-{}^i BuOH]^+$), 625 (27, $[M+Na-AcOH-Ac]^+$), 605 (28, $[M+Na-BzOH]^+$), 597 (16, $[M+Na-{}^i BuOH-Ac]^+$), 579 (18, $[M+Na-{}^i BuOH-AcOH]^+$).

Furan-3-carboxylic Acid rel-*(3*R*,4*R*,5*R*,5a*S*,6*R*,7*S*,9*S*,9a*S*,10*R*)-4,6,7,10-Tetrakis(acetyloxy)octahydro-9-hydroxy-2,2,9-trimethyl-5a-[(2-methyl-1-oxopropoxy)methyl-2*H*-3,9a-methano-1-benzoxepin-5-yl Ester* (**4**): Amorphous white powder. M.p. 269–272°. UV/VIS (MeOH): 230. ^{1}H-NMR ($CDCl_3$): 8.01 (*s*, 1 H (Fu)); 7.44 (*d*, *J* = 2.0, 1 H (Fu)); 6.72 (*d*, *J* = 6.5, 1 H (Fu)); 2.84–2.85 (*m*, Me_2CHCO); 2.19, 2.13, 2.02, 1.68 (4*s*, 4 Ac); 1.63 (*s*, Me(14)); 1.57 (*s*, Me(13)); 1.47 (*s*, Me(15)); 1.27 (*d*, *J* = 6.5, Me_2CHCO). ^{13}C-HMR ($CDCl_3$): 177.8 (Me_2CHCO); 169.7 (2 MeCO); 169.6 (2 MeCO); 160.8 (CO (Fu)); 148.9 (CH (Fu)); 144.0 (CH (Fu)); 117.7 (C (Fu)); 109.6 (CH (Fu)); 35.0 (Me_2CHCO); 21.6 (MeCO); 21.4 (MeCO); 21.1 (MeCO); 20.5 (MeCO); 19.7 (Me_2CHCO); 19.1 (Me_2CHCO). ESI-MS/MS: 689 (3, $[M+Na]^+$, $[C_{32}H_{42}O_{15}+Na]^+$), 629 (100, $[M+Na-AcOH]^+$), 601 (10, $[M+Na-{}^i BuOH]^+$), 587 (12, $[M+Na-AcOH-Ac]^+$), 577 (9, $[M+Na-FuOH]^+$), 569 (9, $[M+Na-2\,AcOH]^+$), 559 (14, $[M+Na-{}^i BuOH-Ac]^+$).

2-Methylbutanoic Acid rel-*[(3*R*,4*R*,5*R*,5a*S*,6*R*,7*S*,9*S*,9a*S*,10*R*)-6,7,10-Tris(acetyloxy)-5-(benzoyloxy)-octahydro-9-hydroxy-2,2,9-trimethyl-4-(2-methyl-1-oxopropoxy)-5a*H*-3,9a-methano-1-benzoxepin-5a-yl]methyl Ester* (**5**): Amorphous white powder. M.p. 94–96°. UV/VIS (MeOH): 243. ^{1}H-NMR ($CDCl_3$): 8.03 (*d*, *J* = 7.2, 2 arom. H); 7.65 (*t*, *J* = 7.5, 1 arom. H); 7.49 (*t*, *J* = 7.5, 2 arom. H); 2.74–2.76 (*m*, Me_2CHCO); 2.72–2.73 (*m*, $MeCH_2CH(Me)CO$); 2.14, 2.13, 1.55 (3*s*, 3 Ac); 1.84–1.86 (*m*, 1 H, $MeCH_2CH(Me)CO$); 1.70 (*s*, Me(14)); 1.57 (*s*, Me(15)); 1.54–1.55 (*m*, 1 H, $MeCH_2CH(Me)CO$); 1.53 (*s*, Me(13)); 1.28 (*d*, *J* = 7.5, 3 H, Me_2CHCO); 1.28 (*d*, *J* = 7.5, $MeCl_2CH(Me)CO$); 1.27 (*d*, *J* = 7.5, 3 H, Me_2CHCO); 0.99 (*t*, *J* = 7.5, $MeCH_2CH(Me)CO$). ^{13}C-HMR ($CDCl_3$): 177.8 (Me_2CHCO); 176.9 ($MeCH_2(Me)CO$); 171.7 (MeCO); 171.2 (MeCO); 171.1 (MeCO); 165.9 (PhCO); 135.0 (CH (Bz)); 131.3 (2 CH (Bz)); 129.8 (2 CH (Bz)); 129.7 (C (Bz)); 42.5 ($MeCH_2CH(Me)CO$); 35.3 (Me_2CHCO); 25.4 ($MeCH_2CH(Me)CO$); 21.3 (MeCO); 21.0 (MeCO); 20.8 (MeCO); 19.5 (Me_2CHCO); 19.3 (Me_2CHCO); 19.3 ($MeCH_2CH(Me)CO$); 17.1 ($MeCH_2CH(Me)CO$). ESI-MS/MS: 741 (18, $[M+Na]^+$, $[C_{37}H_{50}O_{14}+Na]^+$), 681 (100, $[M+Na-AcOH]^+$), 653 (80, $[M+Na-{}^i BuOH]^+$), 639 (51, $[M+Na-{}^i PetOH]^+$, $[M+Na-AcOH-Ac]^+$), 619 (25, $[M+Na-BzOH]^+$), 597 (16, $[M+Na-{}^i PetOH-Ac]^+$), 579 (5, $[M+Na-{}^i PetOH-AcOH]^+$).

REFERENCES

[1] Z.-Q. Ji, Z.-N. Hu, G.-Q. Liu, W.-J. Wu, *Acta Bot. Boreali-Occidentalia Sin*. **2004**, *24*, 748.
[2] W. Wu, M. Wang, J. Zhu, W. Zhou, Z. Hu, Z. Ji, *J. Nat. Prod*. **2001**, *64*, 364.
[3] W. J. Wu, Y. Q. Tu, H. X. Liu, J. B. Zhu, *J. Nat. Prod*. **1992**, *55*, 1294.
[4] Z. Ji, W. Wu, H. Yang, B. Shi, M. Wang, *Nat. Prod. Res.* **2007**, *21*, 334.
[5] Y. L. Zheng, Y. Xu, J. F. Lin, *Acta Pharm. Sin*. **1989**, *24*, 568.
[6] H. Duan, Y. Takaishi, H. Momota, Y. Ohmoto, T. Taki, M. Tori, S. Takaoka, Y. Jia, D. Li, *Tetrahedron* **2001**, *57*, 8413.
[7] Y.-H. Kuo, M.-L. King, C.-F. Chen, H.-Y. Chen, C.-H. Chen, K. Chen, K.-H. Lee, *J. Nat. Prod.* **1994**, *57*, 263.
[8] A. G. González, L. San Andrés, A. G. Ravelo, J. G. Luis, I. A. Jiménez, X. A. Domínguez, *J. Nat. Prod.* **1989**, *52*, 1338.
[9] J. M. Pérez-Victoria, B. M. Tincusi, I. A. Jiménez, I. L. Bazzocchi, M. P. Gupta, S. Castanys, F. Gamarro, A. G. Ravelo, *J. Med. Chem.* **1999**, *42*, 4388.

[10] F. Cortes-Selva, I. A. Jimenez, F. Munoz-Martinez, M. Campillo, I. L. Bazzocchi, L. Pardo, A. G. Ravelo, S. Castanys, F. Gamarro, *Curr. Pharm. Des.* **2005**, *11*, 3125.
[11] F. Cortés-Selva, F. Muñoz-Martínez, A. Iliás, A. I. Jiménez, A. Váradi, F. Gamarro, S. Castanys, *Biochem. Biophys. Res. Commun.* **2005**, *329*, 502.
[12] F. Muñoz-Martínez, P. Lu, F. Cortés-Selva, J. M. Pérez-Victoria, I. A. Jiménez, Á. G. Ravelo, F. J. Sharom, F. Gamarro, S. Castanys, *Cancer Res.* **2004**, *64*, 7130.
[13] K. Ujita, Y. Takaishi, H. Tokuda, H. Nishino, A. Iwashima, T. Fujita, *Cancer Lett*. **1993**, *68*, 129.
[14] Y. Takaishi, K. Ujita, H. Tokuda, H. Nishino, A. Iwashima, T. Fujita, *Cancer Lett*. **1992**, *65*, 19.
[15] A. G. González, C. M. González, I. L. Bozzocchi, A. G. Ravelo, J. G. Luis, X. A. Dominguez, *Phytochemistry* **1987**, *26*, 2133.
[16] K. Yamada, Y. Shizuri, Y. Hirata, *Tetrahedron* **1978**, *34*, 1915.
[17] J.-M. Gao, W.-J. Wu, J.-W. Zhang, Y. Konishi, *Nat. Prod. Rep.* **2007**, *24*, 1153.
[18] A. C. Spivey, M. Weston, S. Woodhead, *Chem. Soc. Rev.* **2002**, *31*, 43.

Received November 3, 2009