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FURANOEREMOPHILANES AND OTHER CONSTITUENTS OF *PITTOCAULON BOMBYCOPHOLE*

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Abstract – Three new eremophilanes (**1**-**3**) and a new oplopane (**4**) were isolated from *Pittocaulon bombycophole*. Additionally, three known sesquiterpenes (**5-7**) and the alkaloid 7-angeloylplatynecine (**8**) were isolated. The structures of the new compounds were elucidated by spectroscopic methods.

INTRODUCTION

The genus *Pittocaulon* (Asteraceae, Senecioneae, Tussilagininae) consists of five species segregated from the genus *Senecio*.[1,2] Four species are endemic to Mexico and one is native of Southern Mexico and Guatemala. All the *Pittocaulon* species grow in dry tropical habitats often on rocky or steep cliffs.[3] Several chemical studies of *Pittocaulon praecox* have shown that it synthesizes furanoeremophilanes as the main secondary metabolites.[4-6] Recently, the pyrrolizidine alkaloids present in the five species of the genus *Pittocaulon* were reported.[7] Considering that there are no studies about non alkaloidal metabolites of *P. bombycophole*, we undertook the chemical study of its roots and stems which afforded four new compounds, three furanoeremophilanes (**1**-**3**) and one oplopane (**4**), as well as four known compounds (**5-8**).[8-13]

RESULTS AND DISCUSSION

Compound **1** was isolated as a pale yellow oil, $[\alpha]_D^{25}$ + 98.3, with the molecular formula $C_{23}H_{32}O_6$, determined by HRFABMS. Its IR spectrum exhibited absorption bands at 1731 and 1688 cm^{-1}, indicative of carbonyl groups, and a band at 792 cm^{-1}, due to furan group. The ^1H and ^{13}C NMR spectra showed

typical signals for a 9-oxofuranoeremophilane: The quartet at δ 7.36 (q, *J* = 1.0 Hz) due to H-12, three signals at δ 1.92 (d, *J* = 1.0 Hz), 0.99 (s), and 0.91 (d, *J* = 6.7 Hz) assigned to H-13, H-14 and H-15, respectively, and the C-9 signal at δ 185.2 The presence of an acetoxy group at C-6 was deduced by the singlet signal at δ 2.19 and the correlation observed in the HMBC experiment between H-6 (δ 6.39) and the ester carbonyl (δ 170.8). The chemical shift of H-3 (δ 4.61) indicated its geminal position to an ester group. This ester was identified as 3-methylpentanoyloxy by the correlations observed in the HMBC experiment between C-1' (δ 172.4) and H-2' and those of C-3' (δ 32.0) with H-2', H-4', H-5' and H-6'. Its MS showed a fragment at *m/z* 288 $[M - C_6H_{12}O_2]^+$ which corresponded to the loss of the methylpentanoic acid. The NOE effects of H-3 with H-14 and H-15, of H-10 with H-4 and H-6, and of H-6 with H-4, suggested the relative stereochemistry depicted in **1** (Figure 1).

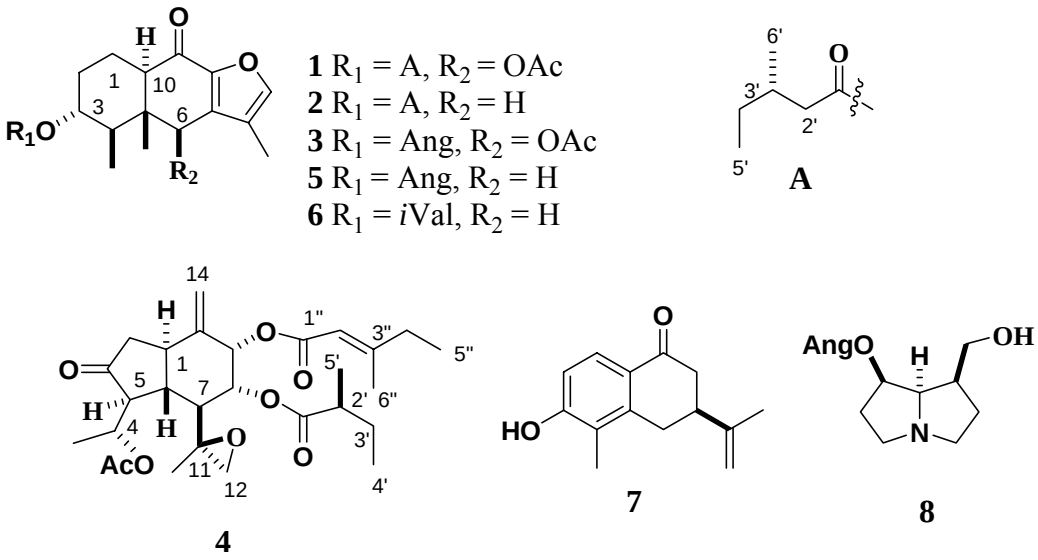

Figure 1

Compound **2** was obtained as colourless crystals, mp 87-90 °C, $[\alpha]_D^{25}$ - 32. The molecular formula $C_{21}H_{30}O_4$ is indicative of seven degrees of unsaturation. Its IR spectrum exhibited bands of carbonyl groups (1728 and 1679 cm^{-1}) and of a furan group (806 cm^{-1}). Its UV spectrum presented an absorption band at 280 nm characteristic of 9-oxofuranoeremophilanes.[14] The ^1H and ^{13}C NMR spectra were similar to those of **1**, except for the absence of the acetyl signals and the presence of an AB system at δ 2.72 and 2.5 in the ^1H NMR spectrum, which was assigned to the hydrogens of the C-6 methylene. The α orientation of the 3-methylpentanoyloxy group was deduced by the NOE interactions of H-3 with H-14 and H-15. The relative stereochemistry was confirmed by an X-Ray crystallographic analysis (Figure 2).

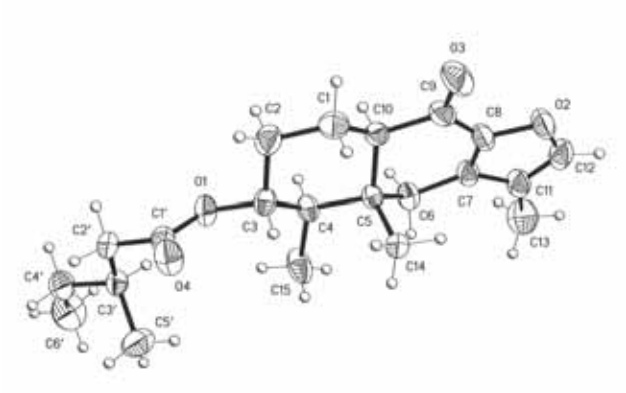

Figure 2. ORTEP projection of 2 (crystallographic numbering)

Compound **3** was isolated as colourless crystals, mp 156-158 ^{o}C, $[\alpha]^{25}_{D}$ - 117.2, and exhibited a molecular formula of $C_{22}H_{28}O_6$. The ^{1}H and ^{13}C NMR spectra were similar to those of **1** except for the presence of an angeloyloxy group (δ 6.06, 1.98, 1.92) instead of a 3-methylpentanoyloxy group. The position of the ester groups was inferred from the HMBC experiment in which the carbonyl of the angeloyloxy group (δ 167.6) showed correlation with H-3 (δ 4.71) and the carbonyl of the acetoxy (δ 170.8) correlated with H-6 (δ 6,40). Considering the interactions observed in the NOESY experiment of H-10 with H-4 and H-6 and those of H-3 with the β orientated methyl groups 14 and 15, compound 3 should have the same stereochemistry as that of **1** and **2**.

Compound **4** was obtained as a white crystalline solid, mp 130-133 ^{o}C. Its molecular formula $C_{28}H_{40}O_8$ was determined by HRMS. The IR spectrum showed bands of saturated and α, β-unsaturated carbonyl groups (1740 and 1717 cm^{-1} respectively). Its ^{1}H NMR spectrum showed the signals of the hydrogen atoms of an exocyclic double bond (δ 4.92 and 5.29) and three signals at δ 5.80, 5.16 and 5.15 which were assigned to hydrogens attached to C-9, C-4 and C-8, respectively, which supported ester functions. These esters were identified as 3-methyl-2-pentenoato, acetate, and 2-methylbutanoate by their characteristic signals observed in the ^{1}H and ^{13}C NMR spectra. The position of the acetoxy group at C-4 (δ 68.6) was achieved by the four-bond correlation observed in the HMBC spectrum between this carbon and the acetyl group (δ 2.11). The position of the 3-methyl-2-pentenoato at C-9 was confirmed by the cross peak observed in the HMBC experiment between H-9 (δ 5.8) and the carbonyl signal at δ 165.3 (C-1"). Therefore, the 2-methylbutanoyloxy group was attached at C-8 (δ 72.8). An epoxy function was localized between C-11 (δ 54.9) and C-12 (δ 52.8) by means of COSY and HMBC experiments. This structure and its relative configuration were established by X-Ray diffraction analysis. The absolute configuration was established by circular dichroism (CD) which showed a negative cotton effect at 303 nm (Δε = - 5. 34) similar to that of the oplopene 14(*R)*-hydroxy-7β-isovaleroyloxyoplop-8(10)-en-2-one

isolated from *Tussilago farfara L.*[15] Based on this evidence, the stereochemistry was determined as 1*R*, 4*R*, 5*S*, 6*R*, 7*S*, 8*R*, 9*S*, 11*S*, 2'*S*, 2"*E* (Figure 3).

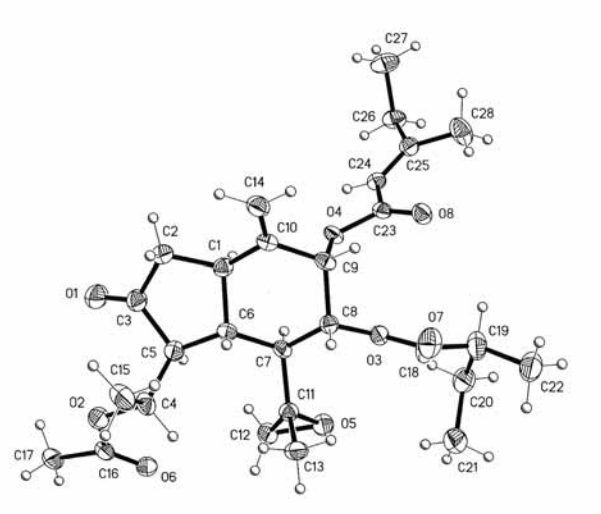

Figure 3. ORTEP projection of 4 (crystallographic numbering)

Structures of the known compounds 3α-angeloyloxy-9-oxofuranoeremophilane (**5**),[8,9] euryopsonol isovalerate (**6**),[10] ligujapone (**7**),[11] and 7-angelylplatynecine (**8**)[12,13] were determined by comparison of their physical constants and spectroscopic features with those reported in literature. The ^{13}C NMR of compound **6** is reported here for the first time.

EXPERIMENTAL

General experimental procedures. Melting points were recorded on a Fisher-Jones apparatus. Optical rotations were determined on a JASCO DIP-360 digital polarimeter. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer. NMR spectra were obtained on an Eclipse JEOL 300 MHz, Bruker Avance 300 MHz or a Varian Unity Inova 500 MHz spectrometer with tetramethylsilane (TMS) as internal standard. EIMS data (70 eV) were determined on a Bruker Daltonics Analysis 3.2 mass spectrometer. FABMS were obtained on a JEOL JMS-SX102A Mass spectrometer and samples were desorbed from a nitro benzyl alcohol matrix using 6 KV xenon atoms. HRFABMS were performed at 10.000 resolution using electric field scans and polyethylene glycol ions (Fluka 200 and 300) as reference material. Column chromatography was carried out under vacuum on Kieselgel G (Merk, Darmstadt, Germany). TLC was performed on Si gel 60 and preparative TLC on Si gel GF_{254} (MERCK) layer thickness 2.0 mm. HPLC separations were carried on Waters Delta Prep. 4000 apparatus, tunable Absorbance Detector Waters 486, λ = 254 nm, RP-column Luna 5 μ C18 (2), 100 Å, 50 x 21.2 mm. X-Ray crystallographic analyses were realized on a Bruker Smart Apex CCD diffractometer with graphite-

monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXS. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions and were not refined.

Plant material. *Pittocaulon bombycophole* (Bullock) H. Rob. & Brettell was collected in Taxco, Guerrero, Mexico, in April 2007. A voucher specimen (MEXU 1205019) was deposited at the herbarium of the Instituto de Biología, Universidad Nacional Autónoma de México.

Extraction and isolation. Dried and ground root bark (441 g) and stem bark (801 g) were extracted exhaustively with hexane and MeOH and the four extracts were concentrated under reduced pressure. The root bark hexane extract (14.09 g) was submitted to column chromatography eluted with hexane-acetone gradient mixture system to obtain 98 fractions. Fractions 15-22 eluted with hexane-acetone (9:1) were submitted to column chromatography using a hexane-acetone gradient mixture system to afford fractions A and B. Fraction A afforded 9 mg of sitosterol-stigmasterol mixture. Purification of B by column chromatography eluted with hexane-acetone gradient system followed of preparative TLC eluted with hexane-EtOAc 9:1 afforded a mixture (110 mg) which was purified by HPLC (H_2O-MeCN) to give 4 mg of **1**. Fractions 27-31 eluted with hexane-acetone 9:1 afforded by crystallization (Et_2O-hexane) a mixture (94 mg), which was submitted to preparative TLC (hexane-acetone 8:2) to yield 11 mg of **7**[11] and 78 mg of compound **4**. Fractions 32-39 eluted with hexane-acetone 9:1 by column chromatography using hexane-acetone gradient system give by crystallization (Et_2O-hexane) 106 mg of **4**. The stem bark hexane extract (33.3 g) was purified by column chromatography with an hexane-acetone gradient mixture system. A portion (1 g) of fractions 30-34 (11.8 g) eluted with hexane-acetone 9:1 was purified by HPLC (MeOH-H_2O 8:2) to afford 47 mg of **5**,[8,9] 12.4 mg of **6**[10] and 130 mg of **2**. Fractions 38-44, eluted with hexane-acetone 9:1, were submitted to column chromatography with an hexane-acetone gradient system to yield 62 fractions from which, the fractions 13-39 eluted with hexane were submitted to column chromatography followed by a preparative TLC both eluted with benzene to afford by crystallization (Et_2O-hexane) 17 mg of **3**. The stem bark methanolic extract (43.5 g) was submitted to column chromatography eluted with EtOAc-MeOH gradient system to obtain 99 fractions. Fractions 46-58 eluted with EtOAc-MeOH 7:3 afforded 18 mg of 7-angeloylplatynecine hydrochloride which on treatment with 0.05 N NaOH gave 10 mg of the free base **8**.[12,13]

6β-Acetoxy-3α-(3'-methylpentanoyloxy)-10α*H*-furanoeremophil-9-one (**1**)**:** Pale yellow oil, $[\alpha]^{20}_D$ - 98 (MeOH, *c* 0.12) UV (MeOH) λ_{max} (log ε) 278 (4.26) nm; IR ($CHCl_3$) ν_{max} 1731, 1688, 792 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36 (1H, q, *J* = 1.0 Hz, H-12), 6.39 (1H, s, H-6), 4.61 (1H, ddd, *J* = 11.0, 11.0, 5.0 Hz, H-3), 2.44 (1H, dd, *J* = 12.5, 3.5, Hz, H-10), 2.29 (1H, ddd, *J* = 14.0, 14.0, 6.5 Hz, H-2'a), 2.27 (1H, m, H-1a), 2.19 (3H, s, OAc), 2.16 (1H, m, H-2a), 2.10 (1H, ddd, *J* = 14.0, 14.0, 6.5 Hz, H-2'b),

1.94 (1H, m, H-4), 1.92 (3H, d, *J* = 1.0 Hz, H-13), 1.88 (1H, m, H-3'), 1.60 (1H, m, H-1b), 1.36 (1H, m, H-4'a), 1.31 (1H, m, H-2b), 1.26 (1H, m, H-4'b), 0.99 (3H, s, H-14), 0.93 (3H, d, *J* = 6.5 Hz, H-6'), 0.91 (3H, d, *J* = 6.7 Hz, H-15), 0.90 (3H, t, *J* = 7.2 Hz, H-5'); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 185.2 (C, C-9), 172.9 (C, C-1'), 170.8 (C, OAc), 146.5 (C, C-7), 145.4 (CH, C-12), 134.7 (C, C-8), 120.8 (C, C-11), 75.3 (CH, C-6), 73.7 (CH, C-3), 54.3 (CH, C-10), 50.0 (C, C-5), 45.9 (CH, C-4), 41.8 (CH_2, C-2'), 32.0 (CH, C-3'), 30.6, (CH_2, C-2), 29.4 (CH_2, C-4'), 21.5 (CH_3, OAc), 19.2 (CH_3, C-6'), 18.9 (CH_2, C-1), 12.0 (CH_3, C-15), 11.2 (CH_3, C-5'), 9.0 (CH_3, C-14), 8.5 (CH_3, C-13). EI-MS *m/z* 404 $[M]^+$ (5), 344 (18), 246 (100), 288 (20), 228 (50); HRFABMS *m/z* 405.2271 (calcd. for $C_{23}H_{33}O_6$, $[M + H]^+$ 405.2277).

3α-(3'-Methylpentanoyloxy)-10α*H*-furanoeremophil-9-one (**2**)**:** Colorless crystals; mp 87-90 °C, $[\alpha]^{20}_D$ - 32 ($CHCl_3$, *c* 0.25) UV (MeOH) λ_{max} (log ε) 280 (4.02) nm; IR ($CHCl_3$) ν_{max} 1728, 1679, 806 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36 (1H, q *J* = 1.2 Hz, H-12), 4.74 (1H, ddd, *J* = 10.8, 10.8, 4.5 Hz, H-3), 2.72 (1H, d, *J* = 16.2 Hz, H-6a), 2.50 (1H, d, *J* = 16.2 Hz, H-6b), 2.41 (d, 1H, dd, *J* = 12.0, 3.6 Hz, H-10), 2.30 (1H, dd, *J* = 14.4, 6.0 Hz, H-2'a), 2.24 (1H, m, H-1a), 2.20 (1H, m, H-2a), 2.12 (1H, dd, *J* = 14.4, 8.1 Hz, H-2'b), 1.99 (3H, d, *J* = 1.2 Hz, H-13), 1.90 (1H, oct, *J* = 6.6 Hz, H-3'), 1.76 (1H, dq, *J* = 10.8, 6.6 Hz H-4), 1.55 (1H, m, H-1b), 1.39 (1H, m, H-4'a), 1.32 (1H, m, H-2b), 1.27 (1H, m, H-4'b), 0.97 (3H, d, *J* = 6.6 Hz, H-15), 0.95 (3H, d, *J* = 6.6 Hz, H-6'), 0.91 (3H, t, *J* = 7.5, Hz, H-5'), 0.86 (3H, s, H-14); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 186.1 (C, C-9), 172.9 (C, C-1'), 146.6 (C, C-7), 144.6 (CH, C-12), 136.5 (C, C-8), 121.2 (C, C-11), 73.7 (CH, C-3), 54.8 (CH, C-10), 47.1 (CH, C-4), 43.9 (C, C-5), 41.8 (CH_2, C-2'), 35.4 (CH_2, C-6), 32.0 (CH, C-3'), 31.1 (CH_2, C-2), 29.4 (CH_2, C-4'), 19.3 (CH_2, C-1), 19.2 (CH_3, C-6'), 13.1 (CH_3, C-14), 11.2 (CH_3, C-5'), 10.5 (CH_3, C-15), 7.7 (CH_3, C-13); EI-MS *m/z* 346 $[M]^+$ (20), 247 (3), 230 (82), 215 (70), 175 (41), 162 (100); HRFABMS *m/z* 347.2221 (calcd. for $C_{21}H_{31}O_4$, $[M + H]^+$ 347.2222).

6β-Acetoxy-3α-angeloyloxy-10α*H*-furanoeremophil-9-one (**3**)**:** colourless crystals; mp 156-158 °C, $[\alpha]^{20}_D$ – 117 ($CHCl_3$, *c* 0.25) UV (MeOH) λ_{max} (log ε) 278 (4.32) nm; IR ($CHCl_3$) ν_{max} 1746, 1683, 851 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz ,) δ 7.37 (1H, q, *J* = 1.2 Hz, H-12), 6.40 (1H, s, H-6), 6.06 (1H, qq, *J* = 7.2, 1.5 Hz, H-3'), 4.71 (1H, ddd, *J* = 10.8, 10.8, 4.5 Hz, H-3), 2.47 (1H, dd, *J* = 12.0, 3.5, Hz, H-10), 2.31 (1H, dddd, *J* = 12.5, 12.0, 7.0, 3.5 Hz, H-1a), 2.23 (1H, dddd, *J* = 12.5, 8.0, 4.0, 3.5 Hz, H-2a), 2.19 (3H, s, OAc), 2.02 (1H, m, H-4), 1.98 (3H, dq, *J* = 7.2, 1.5 Hz, H-4'), 1.92 (3H, d, *J* = 1 Hz, H-13), 1.88 (3H, quint, *J* = 1.5 Hz, H-5'), 1.62 (1H, m, H-1b), 1.36 (1H, m, H-2b), 1.02 (3H, s, H-14), 0.94 (3H, d, *J* = 6.6 Hz, H-15); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 185.2 (C, C-9), 170.8 (C, OAc), 167.6 (C, C-1'), 146.5 (C, C-8), 145.4 (CH, C-12), 137.8 (CH, C-3'), 134.7 (C, C-7), 127.9 (C, C-2'), 120.9 (C, C-11), 75.3 (CH, C-6), 73.6 (CH, C-3), 54.4 (CH, C-10), 50.1 (C, C-5), 46.1 (CH, C-4), 30.8 (CH_2 C-2), 21.5 (CH_3, OAc), 20.5 (CH_3, C-4'), 19.0 (CH_2, C-1), 15.7 (CH_3, C-5'), 12.1 (CH_3, C-15), 8.9 (CH_3, C-14), 8.5 (CH_3, C-13); EI-

MS *m/z* 388 $[M]^+$ (3), 328 (20), 288 (20), 246 (75), 228 (63), 138 (38), 83 (100), 55 (45); HRFABMS *m/z* 389.1975 (calcd. for $C_{22}H_{29}O_6$, $[M+H]^+$ 389.1964).

(1*R*, 4*R*, 5*S*, 6*R*, 7*S*, 8*R*, 9*S*, 11*S*, 2'*S*, 2"*E*)-11,12-Epoxy-8-(2'-methylbutanoyloxy)-9-(3"-methyl-2"-pentenoyloxy)-10(14)-oplopen-3-one (**4**)**:** white crystals mp 130-133 °C, $[\alpha]_D^{20}$ + 15.4 ($CHCl_3$, *c* 0.23); UV (MeOH) λ_{max} (log ε) 220 (4.32) nm; IR (KBr) ν_{max} 1740, 1717, 1651 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.80 (1H, d, *J* = 3.3 Hz, H-9), 5.64 (1H, d, *J* = 1.2 Hz, H-2"), 5.29 (1H, d, *J* = 1.5 Hz, H-14a), 5.16 (1H, m, H-4), 5.15 (1H, m, H-8), 4.92 (1H, d, *J* = 1.5 Hz, H-14b), 2.81 (1H, d, *J* = 3.9 Hz, H-12a), 2.69 (1H, d, *J* = 3.9 Hz, H-12b), 2.64 (1H, brd, *J* = 11.5 Hz, H-5), 2.5 (1H, ddd, *J* = 17.0, 7.0, 1.0 Hz, H-1), 2.42 (1H, dd, *J* = 14.0, 7.0 Hz, H-2a), 2.42 (1H, m, H-2'), 2.18 (1H, m, H-2b), 2.18 (2H, m, H-4"), 2.13 (3H, d, *J* = 1.2 Hz, H-6"), 2.11 (3H, s, OAc), 2.01 (1H, m, H-7), 1.76 (1H, ddq, *J* = 14.3, 7.0, 7.0 Hz, H-3'a), 1.53 (1H, brdd, *J* = 11.5, 11.5 Hz, H-6), 1.48 (1H, ddq, *J* = 14.3, 7.0, 7.0, Hz, H-3'b), 1.25 (3H, s, H-13), 1.23 (3H, d, *J* = 7.0 Hz, H-15), 1.17 (3H, d, *J* = 7.2 Hz, H-5'), 1.07 (3H, t, *J* = 7.2 Hz, H-5"), 0.91 (3H, t, *J* = 7.2 Hz, H-4'); ^{13}C NMR ($CDCl_3$, 75.4 MHz,): δ 212.6 (C, C- 3), 176.1 (C, C-1'), 170.7 (C, OAc), 165.3 (C, C- 1"), 163.1 (C, C-3"), 142.3 (C, C-10), 113.9 (CH, C-2"), 113.0 (CH_2, C-14), 72.8 (CH, C-8), 72.2 (CH, C-9), 68.6 (CH, C-4), 56.4 (CH, C-5), 54.9 (C, C-11), 52.8 (CH_2, C-12), 48.8 (CH, C-7), 45.8 (CH, C-6), 41.8 (CH_2, C-2), 41.1 (CH, C-2'), 40.9 (CH_2, C-1), 33.8 (CH_2, C-4"), 26.3 (CH_2, C-3'), 21.3 (CH_3, OAc), 18.9 (CH_3, C-6"), 16.2 (CH_3, C-5'), 15.9 (CH_3, C-13), 15.1 (CH_3, C-15), 11.8 (CH_3, C-5"), 11.6 (CH_3, C- 4'); EIMS *m/z* 504 $[M]^+$ (2), 403 (5), 246 (5), 228 (8), 97 (100), 57 (24); HRFABMS *m/z* : 505.2795 (calcd. for $C_{28}H_{41}O_8$, $[M + H]^+$ 505.2801).

Euryopsonol isovalerate (**6**)**:** white crystal mp 109-111 °C; ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 186.2 (C, C-9), 172.8 (C, C-1'), 146.6 (C, C-8), 144.6 (CH, C-12), 136.5 (C, C-11), 121.2 (C, C-7), 73.7 (CH, C-3), 54.8 (CH, C-10), 47.1 (CH, C-4), 43.9 (C, C-5), 43.8 (CH_2, C-2'), 35.4 (CH_2, C-6), 31.1 (CH_2, C-2), 25.8 (CH, C-3'), 22.5 (CH_3, C-4'), 22.4 (CH_3, C-5'), 19.4 (CH_2, C-6), 13.1 (CH_3, C-14), 10.5 (CH_3, C-15), 7.8 (CH_3, C-13).

Crystal data of 2: $C_{21}H_{30}O_4$, M_r 346.45, monoclinic, space group $P2_1$, a = 7.801 (1) Å, α = 90.00°, b = 12.905 (2) Å, β = 91.899 (2)°, c = 9.907 (1) Å; γ = 90°, V = 996.7(2) $Å^3$, Z = 2, D_c = 1.154 Mg/m^3, F(000) = 376; crystal dimensions 0.466 x 0.178 x 0.108 mm. Reflections collected 9793, independent reflections 2391. Number of parameters refined 226; final R indices (observed data) R = 4.62 %, wR^2 = 9.3 %; R indices (all data) R = 7.12 %, wR^2 10.1 %.

Crystal data of 4: $C_{28}H_{40}O_8$, M_r 504.60, orthorhombic, space group $P2_12_12_1$, a = 6.578 (2) Å, α = 90.00°, b = 14.847 (5) Å, β = 90°, c = 28.496 (10) Å; γ = 90°, V = 2783.3(17) $Å^3$, Z = 4, D_c = 1.204 Mg/m^3, F(000) = 1088; crystal dimensions 0.56 x 0.07 x 0.05 mm. Reflections collected 26404, independent reflections 2962. Number of parameters refined 399; final R indices (observed data) R = 5.13 %, wR^2 =

11.32 %; *R* indices (all data) *R* = 9.15 %, wR^2 12.96 %. Crystallographic data for **2** (CCDC-697746) and **4** (CCDC-697747) are available free of charge via the Internet at http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: + 441223336033; deposit@ccdc.cam.ac.uk).

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