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# CYCLOARTANE TRITERPENES FROM THE FRUIT PEEL OF *MUSA SAPIENTUM*

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**Key Word Index**—*Musa sapientum*; Musaceae; banana peel; triterpene; cycloartane.

**Abstract**—Five novel cycloartane-type triterpenes were isolated from the nonsaponifiable lipids obtained from the methanol extract of the fruit peel of *Musa sapientum* L. (banana). Their structures were determined to be 3-epicycloeucalenol, 3-epicyclomusalenol, 24-methylenepollinastanone, 28-norcyclomusalenone and 24-oxo-29-norcycloartanone by spectroscopic and chemical methods. © 1998 Elsevier Science Ltd. All rights reserved

## INTRODUCTION

The lipids of the fruit peel of banana (*Musa sapientum* L.) characteristically contain considerable amounts of two 3-oxo-29-norcycloartane-type triterpenes, cycloeucalenone [24-methyl-29-norcycloart-24(24$^1$)-en-3-one; **4a**] and cyclomusalenone [(24*S*)-24-methyl-29-norcycloart-25-en-3-one; **4b**] [1, 2]. Our recent investigation on the 3-oxotriterpene fraction led to the isolation and characterization of two 3-oxo-28-norcycloartane-type triterpenes, 4-epicycloeucalenone [24-methyl-28-norcycloart-24(24$^1$)-en-3-one] and 4-epicyclomusalenone [(24*S*)-24-methyl-28-norcycloart-25-en-3-one], the 4$\beta$-methyl-isomers of the above two 29-norcycloartanes, respectively [3]. In the present paper, we report on the isolation and characterization of five novel cycloartane-type triterpenes, **1a**, **1b**, **3a**, **3b** and **4c**, from the nonsaponifiable lipids of the methanol extract of banana peel.

## RESULTS AND DISCUSSION

Column chromatography on silica gel followed by argentation TLC and reversed-phase HPLC of the nonsaponifiable lipid obtained by alkaline hydrolysis from the methanol extract of the dried banana peel yielded five cycloartane-type triterpenes, **1a**, **1b**, **3a**, **3b** and **4c**.

The IR spectrum of **1a** indicated the presence of a hydroxyl group (3428 cm$^{-1}$), a terminal methylene group (3079, 1641 and 887 cm$^{-1}$) and a cyclopropyl group (3032 cm$^{-1}$). The mass spectrum of **1** showed $[M]^+$ at *m/z* 426 ($C_{30}H_{50}O$) accompanied with diagnostic fragment ions at *m/z* 408 $[M-H_2O]^+$, 342 $[M-C_6H_{12}$ {part of side-chain (s.c.)}$]^+$, 301 $[M-C_9H_{17}$ (s.c.)$]^+$, 300 $[M-C_8H_{14}O$ (ring A)$]^+$, 259 $[M-C_{12}H_{23}$ (ring D+s.c.)$]^+$ and 245 (*m/z* 259-$CH_2$) which were almost indistinguishable from those of cycloeucalenol [24-methyl-29-norcycloart-24(24$^1$)-en-3$\beta$-ol; **2a**] [1, 4]. Compound **1a** showed a hydroxymethine signal at $\delta$ 3.83 as a broad singlet ($W_{1/2}$ = 9 Hz) in the $^1$H NMR spectrum suggesting that it possessed an axially oriented hydroxyl group [5]. The other $^1$H signals of **1a** were similar to those of **2a** [6] and, hence, **1a** was considered to be a stereoisomer at C-3 of **2a**, i.e., 24-methyl-29-norcycloart-24(24$^1$)-en-3$\alpha$-ol [4$\alpha$,14$\alpha$-dimethyl-9$\beta$,19-cycloergost-24(24$^1$)-en-3$\alpha$-ol; 3-epicycloeucalenol], which was confirmed by chemical correlation with cycloeucalenone (**4a**). Thus, $LiAlH_4$ reduction of **4a** yielded **1a**, in addition to **2a**, which was identical by chromatographic and spectral comparison with natural **1a**.

The IR spectrum of compound **1b** showed the presence of a hydroxyl group (3445 cm$^{-1}$), a terminal methylene group (3069, 1645 and 886 cm$^{-1}$) and a cyclopropyl group (3033 cm$^{-1}$). The mass spectrum displayed $[M]^+$ at *m/z* 426 ($C_{30}H_{50}O$) accompanied with diagnostic fragment ions at *m/z* 408 $[M-H_2O]^+$, 356 $[M-C_5H_{10}$ (part of s.c.)$]^+$, 301 $[M-C_9H_{17}$ (s.c.)$]^+$, 300 $[M-C_8H_{14}O$ (ring A)$]^+$. 259 $[M-C_{12}H_{23}$ (ring D+s.c.)$]^+$ and 245 (*m/z* 259-$CH_2$) which were almost indistinguishable from those of cyclomusalenol [(24*S*)-24-methyl-29-norcycloart-25-en-3$\beta$-ol; **2b**] [1]. The skeletal and side chain $^1$H signals in the $^1$H NMR spectrum (see Experimental Section) of **1b** were quite similar to the corresponding signals of **1a** and **2b** [2], respectively, and, hence **1b** appeared to be (24*S*)-24-methyl-29-norcycloart-25-en-3$\alpha$-ol [(24*S*)-4$\alpha$,14$\alpha$-

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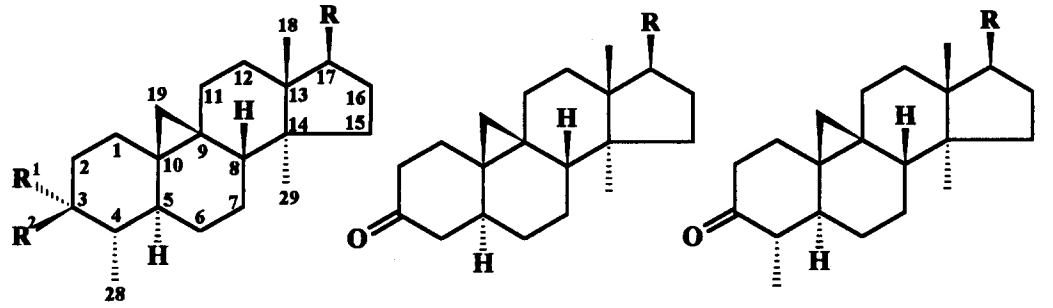
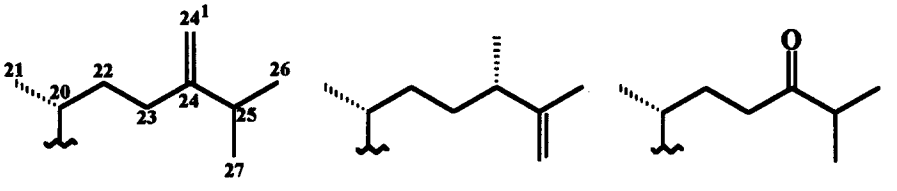


**1** $R^1 = OH$ $R^2 = H$
**2** $R^1 = H$ $R^2 = OH$

**3** **4**

**Side chain (R)**



**a** **b** **c**

Structure 1.

dimethyl-9$\beta$,19-cycloergost-25-en-3$\alpha$-ol; 3-epicyclomusalenol]. This was confirmed by its synthesis from **4b** by $LiAlH_4$ reduction. The semi-synthetic **1b** was identical by chromatographic and spectral comparison with natural **1b**.

The IR spectrum of **3a** showed the presence of an oxo group (1719 $cm^{-1}$), a terminal methylene group (3084, 1637 and 885 $cm^{-1}$), a cyclopropyl group (3040 $cm^{-1}$) and no hydroxyl group. Its mass spectrum showed $[M]^+$ at *m/z* 410 ($C_{29}H_{46}O$) accompanied with diagnostic fragment ions at *m/z* 395 $[M\text{-}Me]^+$, 367 $[M\text{-}C_3H_7$ ($C_{25} \sim C_{27}$)$]^+$, 326 $[M\text{-}C_6H_{12}$ (part of s.c.)$]^+$, 300 $[M\text{-}C_7H_{10}O$ (ring A)$]^+$, 285 $[M\text{-}C_9H_{17}$ (s.c.)$]^+$, 243 $[M\text{-}C_{12}H_{23}$ (ring D+s.c.)$]^+$ and 229 (*m/z* 243-$CH_2$). This implied that **3a** possesses a 24-methylene-substituted $C_9$-side chain attached to a C-14 methylated 3-oxo-9$\beta$,19-cyclosteroid nucleus. The skeletal $^1H$ signals observed in the $^1H$ NMR spectrum of **3a** at $\delta$ 1.00 (3H, *s*, $H_3$-18), 0.35 and 0.61 (each 1H and *d*, $H_2$-19), and 0.92 (3H, *s*, $H_3$-30) were consistent with the corresponding signals for cyclopholidone (14$\alpha$,24,24-trimethyl-9$\beta$,19-cyclocholest-25-en-3-one) [7], whereas its side chain signals at $\delta$ 0.91 (3H, *d*, $H_3$-21), 1.03 and 1.04 (each 3H and *d*, $H_3$-26 and $H_3$-27), and 4.67 (1H, *d*, $J$ = 1.5 Hz) and 4.72 (1H, *br s*) ($H_2$-24$^1$) were very close to the corresponding signals of **1a**. Based on the spectral evidence cited above, **3a** was considered to have the structure 14$\alpha$-methyl-9$\beta$,19-cycloergost-24(24$^1$)-en-3-one (24-methylenepollinastanone).

Compound **3b** displayed the IR absorptions due to an oxo group (1718 $cm^{-1}$), a terminal methylene group (3077, 1644 and 896 $cm^{-1}$), a cyclopropyl group (3040 $cm^{-1}$) and no hydroxyl group. Its mass spectrum showed $[M]^+$ at *m/z* 410 ($C_{29}H_{46}O$) accompanied with diagnostic fragment ions at *m/z* 395 $[M\text{-}Me]^+$, 340 $[M\text{-}C_5H_{10}$ (part of s.c.)$]^+$, 300 $[M\text{-}C_7H_{10}O$ (ring A)$]^+$, 285 $[M\text{-}C_9H_{17}$ (s.c.)$]^+$, 243 $[M\text{-}C_{12}H_{23}$ (ring D+s.c.)$]^+$ and 229 (*m/z* 243-$CH_2$). The skeletal $^1H$ signals of **3b** in the $^1H$ NMR spectrum were almost identical with the corresponding signals of **3a**, whereas the side-chain $^1H$ signals [$\delta$ 0.87 (3H, *d*, $H_3$-21), 1.64 (3H, *s*, $H_3$-26), 4.67 (2H, *br s*, $H_2$-27) and 1.00 (3H, *d*, $H_3$-24$^1$)] were very close to those observed for **1b**. Based on these spectral evidence, we concluded that **3b** had the structure (24*S*)-14$\alpha$-methyl-9$\beta$,19-cycloergost-25-en-3-one (28-norcyclomusalenone).

The IR spectrum of **4c** showed the presence of an oxo group (1712 $cm^{-1}$) and cyclopropyl group (3040 $cm^{-1}$) and no hydroxyl group. Its mass spectrum showed $[M]^+$ at *m/z* 426 ($C_{29}H_{46}O_2$) accompanied with diagnostic fragment ions at *m/z* 411 $[M\text{-}Me]^+$, 340 $[M\text{-}C_5H_{10}O$ (part of s.c.)$]^+$, 302 $[M\text{-}C_8H_{12}O$ (ring A)$]^+$, 299 $[M\text{-}C_8H_{15}O$ (s.c.)$]^+$, 257 $(M\text{-}C_{11}H_{21}O$ (ring D+s.c.)$]^+$ and 243 (*m/z* 257-$CH_2$). The skeletal $^1H$ signals [$\delta$ 1.00 (3H, *s*, $H_3$-18), 0.40 and 0.62 (each 1H and *d*, $H_2$-19), 0.99 (3H, *d*, $H_3$-28), and 0.91 (3H, *s*, $H_3$-30)] in the $^1H$ NMR spectrum of **4c** were in agreement with the corresponding signals for **4a** [2], whereas its side chain $^1H$ signals [$\delta$ 0.87 (3H, *d*, $H_3$-21), 2.62 (1H, *sept.*, H-25) and 1.10 (6H, *d*, $H_3$-26 and $H_3$-27)] were consistent with those of 24-oxocy-

cloartanyl acetate [24-oxocycloartan-3$\beta$-yl acetate] [7]. The combined evidence confirmed that **4c** was 24-oxo-29-norcycloartan-3-one (24-oxo-9$\beta$,19-cyclo-4$\alpha$, 14$\alpha$-dimethylcholestan-3-one; 24-oxo-29-norcycloartanone).

The five cycloartane-type triterpenes, **1a**, **1b**, **3a**, **3b** and **4c**, described above are considered to be new natural products. The $^1$H NMR data for the five cycloartanes, and the $^{13}$C NMR data for **1a**, **1b** and **3a** are shown in the Experimental Section.

## EXPERIMENTAL

*General.* Crystallizations were performed in $Me_2CO$–MeOH. Mp: uncorr; Prep (0.5 mm thick) $Ag^+$-TLC: silica gel–$AgNO_3$ (4:1) developed $\times 2$ with $CCl_4$–$CH_2Cl_2$ (4:1); HPLC: $C_{18}$ silica column [Superiorex ODS S-5 $\mu$m column, 25 cm $\times$ 10 mm i.d. (Shiseido Co., Tokyo), temp. 25°], MeOH as mobile phase (flow rate 4 ml min$^{-1}$); GC: DB-17 fused-silica capillary column (30 m $\times$ 0.3 mm i.d.), column temp. 275°. $RR_t$ on HPLC and GC expressed relative to cholest-5-en-3$\beta$-ol (cholesterol). IR: KBr discs; EI MS (70 eV): probe; $^1$H NMR (400 MHz) and $^{13}$C NMR (100.6 MHz): $CDCl_3$ with TMS ($^1$H NMR) and $CDCl_3$ at $\delta$ 77.0 ($^{13}$C NMR) as int. standard. The $^1$H and $^{13}$C NMR signal assignments for **1a**, **1b** and **3a** were performed by comparison with the lit. data for **2a** [6], and further with the aid of following NMR experiments: $^{13}$C DEPT, $^1$H-$^1$H COSY, $^1$H-$^{13}$C COSY, HMBC and NOE spectroscopy. Banana, which was free of post-harvest agricultural chemicals and imported from Philippines, was purchased at a market in Tokyo. Cycloeucalenone (**4a**) [2, 3] and cyclomusalenone (**4b**) [2, 3] were used in this study for the prepn of reference compounds of **1a** and **1b**, respectively.

*Isolation procedure.* Banana peel (2.75 kg) was air-dried and the tissue (280 g) was extracted at room temp. $\times 3$ for 3 days each with MeOH. The non-saponifiable lipid (4.42 g) obtained from the MeOH extract (71 g) by alkaline hydrolysis (5% KOH in MeOH, reflux 3 hr) were subjected to CC on silica gel (250 g) with *n*-hexane and *n*-hexane–EtOAc (18:1, 9:1 and 4:1) as eluents. The residue of the *n*-hexane–EtOAc (18:1) eluate, after rechromatography over silica gel, yielded a fr. (1.8 g) which was constituted mainly with **4a** [2] followed by **4b** [2]. This, upon further chromatography on prep. $Ag^+$-TLC, yielded two frs: one (1.3 g), recovered from the less-polar band, was a mixt. of **4a** and **4b**, and the other (80 mg), from the more-polar band, was a mixt. of several compounds. Prep. HPLC of the fr. from the more-polar band gave **1a** (2.5 mg), **1b** (2.0 mg), **3a** (2.7 mg), **3b** (0.4 mg) and **4c** (1.2 mg).

*3-Epicycloeucalenol* (**1a**). Mp 99–101°, $RR_t$: 0.97 (HPLC), 1.74 (GC). IR $\nu_{max}$ cm$^{-1}$: 3428 (OH), 3079, 1641, 887 (>C=$CH_2$), 3032 (cyclopropyl); MS *m/z* (rel. int.): 426 (13) $[M]^+$, 411 (18), 408 (39), 393 (29), 383 (2), 353 (3), 343 (2), 342 (2), 327 (2), 325 (2), 309 (2), 301 (10), 300 (16), 285 (5), 283 (6), 273 (3), 269 (3), 259 (2), 257 (3), 245 (6), 243 (2), 241 (4), 227 (4), 55 (100); HRMS *m/z*: 426.3882 ($C_{30}H_{50}O$ $[M]^+$, requires 426.3859), 408.3742 ($C_{30}H_{48}$), 393.3486 ($C_{29}H_{45}$), 342.2949 ($C_{24}H_{38}O$), 301.2697 ($C_{21}H_{33}O$), 300.2781 ($C_{22}H_{36}$), 259.2196 ($C_{18}H_{27}O$), 245.2038 ($C_{17}H_{25}O$); NMR $\delta_C$ and $\delta_H$: C-1 [26.8; 1.06 ($\beta$), 1.84 ($\alpha$)], C-2 [33.0; 1.67 ($\beta$), 1.80 ($\alpha$)], C-3 [72.3; 3.83 (*br s*, $W_{1/2}$ = 9 Hz)], C-4 [41.0; 1.42], C-5 [37.9; 1.66], C-6 [24.5; 0.55 (*dq*, *J* = 2.9, 12.5 Hz; $\beta$), 1.55 ($\alpha$)], C-7 [24.8; 1.10 ($\alpha$), 1.28 ($\beta$)], C-8 [46.9; 1.60], C-9 [23.2], C-10 [30.2], C-11 [26.9, 1.22 ($\beta$), 1.98 ($\alpha$)], C-12 [32.9; 1.63 (2H)], C-13 [45.3], C-14 [49.0], C-15 [35.3; 1.30 (2H)], C-16 [28.2; 1.31 ($\beta$), 1.92 ($\alpha$)], C-17 [52.2; 1.61], C-18 [17.8; 0.97 (*s*)], C-19 [26.2; 0.10 (*d*, *J* = 4.1 Hz; *exo*), 0.37 (*d*, *J* = 3.9 Hz; *endo*)], C-20 [36.2; 1.41], C-21 [18.3; 0.90 (3H, *d*, *J* = 6.1 Hz)], C-22 [35.0; 1.15, 1.57], C-23 [31.3; 1.90, 2.12], C-24 [157.0], C-25 [33.8; 2.24 (*sept.*, *J* = 6.9 Hz)], C-26 and C-27 [21.9, 22.0; 1.03 (6H, *d*, *J* = 6.9 Hz)], C-24$^1$ [105.9; 4.67 (*br s*), 4.71 (*br s*)], C-28 [15.5; 0.94 (3H, *d*, *J* = 6.9 Hz)], C-30 [19.1; 0.91 (3H, *s*)].

*Preparation of 3-epicycloeucalenol* (**1a**) *from cycloeucalenone* (**4a**). Reduction of **4a** (50 mg) with $LiAlH_4$ (100 mg) in dry THF (10 ml) under $N_2$ at room temp. for 3 hr followed by the usual work-up and HPLC yielded **1a** (7 mg) and cycloeucalenol (**2a**) [2] (33 mg). Semi-synthetic **1a** was identical by chromatographic and spectral comparison with the natural product (**1a**).

*3-Epicyclomusalenol* (**1b**). Mp 121–122°, $RR_t$: 0.94 (HPLC), 1.70 (GC). IR $\nu_{max}$ cm$^{-1}$: 3445 (OH), 3069, 1645, 886 (>C=$CH_2$), 3033 (cyclopropyl); MS *m/z* (rel. int.): 426 (25) $[M]^+$, 411 (37), 408 (5), 393 (4), 356 (2), 328 (2), 301 (15), 300 (22), 285 (7), 283 (8), 259 (3), 245 (6), 233 (4), 227 (3), 215 (6), 201 (10), 55 (100); HRMS *m/z*: 426.3864 ($C_{30}H_{50}O$ $[M]^+$, requires 426.3859), 408.3717 ($C_{30}H_{48}$), 356.3044 ($C_{25}H_{40}O$), 301.2639 ($C_{21}H_{33}O$), 300.2758 ($C_{22}H_{36}$), 259.2194 ($C_{18}H_{27}O$), 245.2052 ($C_{17}H_{25}O$); NMR $\delta_C$ and $\delta_H$: C-1 [26.8; 1.06 ($\beta$), 1.83 ($\alpha$)], C-2 [33.0; 1.68 ($\beta$), 1.84 ($\alpha$)], C-3 [72.3; 3.83 (*br s*, $W_{1/2}$ = 9 Hz)], C-4 [41.0; 1.44], C-5 [37.9; 1.66], C-6 [24.5; 0.55 (*dq*, *J* = 2.9, 12.5 Hz, $\beta$), 1.56 ($\alpha$)], C-7 [24.8; 1.10 ($\alpha$), 1.30 ($\beta$)], C-8 [46.9; 1.61], C-9 [23.2], C-10 [30.2], C-11 [26.9; 1.20 ($\beta$), 1.97 ($\alpha$)], C-12 [32.9; 1.62 (2H)], C-13 [45.3], C-14 [49.0], C-15 [35.3; 1.29 (2H)], C-16 [28.0; 1.27 ($\beta$), 1.89 ($\alpha$)], C-17 [52.2; 1.58], C-18 [17.7; 0.96 (*s*)], C-18 [26.2; 0.10 (*d*, *J* = 3.7 Hz; *exo*), 0.37 (*d*, *J* = 3.7 Hz; *endo*)], C-20 [36.1; 1.36], C-21 [18.4; 0.86 (*d*, *J* = 6.6 Hz)], C-22 [33.9; 0.96, 1.34], C-23 [31.5; 1.17, 1.41], C-24 [41.6; 2.09 (*hextet* like, *J* = 7.0 Hz)], C-25 [150.3], C-26 [18.6; 1.64 (*t*, *J* = 1.4 Hz)], C-27 [109.7; 4.67 (*t*, *J* = 1.4 Hz), C-24$^1$ [20.2; 1.00 (*d*, *J* = 6.9 Hz)], C-28 [15.5; 0.94 (*d*, *J* = 7.1 Hz)], C-30 [19.1; 0.89 (*s*)].

*Preparation of 3-epicyclomusalenol* (**1b**) *from cyclomusalenone* (**4b**). Reduction of **4b** (25 mg) with $LiAlH_4$ (50 mg) in dry THF (10 ml) under $N_2$ at room temp. for 3 hr followed by the usual work-up and HPLC yielded **1b** (2 mg) and cyclomusalenol (**2a**) [2] (9 mg).

Semi-synthetic **1b** was identical by chromatographic and spectral comparison with the natural product (**1b**).

24-*Methylenepollinastanone* (**3a**). Mp 65–67°, $RR_t$: 0.83 (HPLC), 1.78 (GC). IR $\nu_{max}$ $cm^{-1}$: 1719 (>C=O), 3084, 1637, 885 (>C=$CH_2$), 3040 (cyclopropyl); MS *m/z* (rel. int.): 410 (20) $[M]^+$, 395 (7), 367 (10), 327 (9), 326 (9), 313 (7), 311 (4), 301 (2), 300 (2), 285 (20), 283 (7), 273 (3), 258 (3), 243 (5), 229 (3), 219 (8), 55 (100); HR MS *m/z*: 410.3547 ($C_{29}H_{46}O$ $[M]^+$, requires 410.3546), 395.3323 ($C_{28}H_{43}O$), 326.2571 ($C_{23}H_{34}O$), 300.2854 ($C_{22}H_{36}$), 285.2225 ($C_{20}H_{29}O$), 243.1788 ($C_{17}H_{23}O$), 229.1677 ($C_{16}H_{21}O$); NMR $\delta_C$ and $\delta_H$: C-1 [32.1; 1.61 (*β*), 1.90 (α)], C-2 [41.3; 2.39 (2H)], C-3 [212.9], C-4 [48.5; 2.16, 2.29], C-5 [39.8; 1.95], C-6 [28.4; 0.82 (*dq*, *J* = 3.2, 12.4 Hz; *β*), 1.50 (α)], C-7 [24.9; 1.18 (α), 1.37 (*β*)], C-8 [46.9; 1.72], C-9 [24.5], C-10 [29.2], C-11 [27.2; 1.31 (*β*), 2.04 (α)], C-12 [32.7; 1.67 (2H)], C-13 [45.4], C-14 [48.9], C-15 [35.3; 1.34 (2H)], C-16 [28.1; 1.33 (*β*), 1.98 (α)], C-17 [52.2; 1.64], C-18 [17.8; 1.00 (*s*)], C-19 [25.9; 0.35 (*d*, *J* = 4.0 Hz; *exo*), 0.61 (*d*, *J* = 0.61; *endo*)], C-20 [36.1; 1.42], C-21 [18.3; 0.91 (*d*, *J* = 7.1 Hz)], C-22 [35.0; 1.16, 1.58], C-23 [31.3; 1.88, 2.14], C-24 [156.9], C-25 [33.8; 2.24 (*sept.*, *J* = 6.6 Hz)], C-26 and C-27 [21.9, 22.0; 1.03 (*d*, *J* = 7.0 Hz), 1.04 (*d*, *J* = 7.0 Hz)], C-24$^1$ [106.0; 4.67 (*d*, *J* = 1.5 Hz), 4.72 (*br s*)], C-30 [19.1; 0.92 (*s*)].

28-*Norcyclomusalenone* (**3b**). $RR_t$: 0.82 (HPLC), 1.75 (GC). IR $\nu_{max}$ $cm^{-1}$: 1718 (>C=O), 3077, 1644, 896 (>C=$CH_2$), 3040 (cyclopropyl); MS *m/z* (rel. int.): 410 (24) $[M]^+$, 395 (9), 340 (4), 327 (3), 314 (5), 313 (5), 312 (5), 301 (3), 300 (3), 285 (34), 275 (3), 273 (3), 271 (3), 245 (5), 243 (5), 229 (7), 219 (7), 217 (6), 215 (6), 203 (7), 189 (9), 55 (100); HRMS *m/z*: 410.3532 ($C_{29}H_{46}O$ $[M]^+$, requires 410.3546), 395.3342 ($C_{28}H_{43}O$), 340.2708 ($C_{24}H_{36}O$), 300.2769 ($C_{22}H_{36}$), 285.2214 ($C_{20}H_{29}O$), 243.1799 ($C_{17}H_{23}O$), 229.1673 ($C_{16}H_{21}O$); $^1$H NMR: $\delta$ 0.34 (1H, *d*, *J* = 4.4 Hz, H-19 *exo*), 0.61 (1H, *d*, *J* = 4.0 Hz, H-19 *endo*), 0.87 (3H, *d*, *J* = 6.6 Hz, $H_3$-21), 0.91 (3H, *s*, $H_3$-30), 0.99 (3H, *s*, $H_3$-18), 1.00 (3H, *d*, *J* = 6.9 Hz, $H_3$-24$^1$), 1.64 (3H, *br s*, $H_3$-26), 2.10 (1H, *hextet* like, *J* = 7.0 Hz, H-24), 4.67 (2H, *br s*, $H_2$-27).

24-*Oxo*-28-*norcycloartanone* (**4c**). $RR_t$: 0.32 (HPLC), 3.14 (GC). IR $\nu_{max}$ $cm^{-1}$: 1712 (>C=O), 3040 (cyclopropyl); MS *m/z* (rel. int.): 426 (23) $[M]^+$, 411 (7), 340 (12), 325 (2), 302 (5), 299 (27), 287 (2), 257 (3), 243 (3), 221 (6), 136 (21), 43 (100); HRMS *m/z*: 426.3471 ($C_{29}H_{46}O_2$ $[M]^+$, requires 426.3495), 411.3264 ($C_{28}H_{43}O_2$), 340.2760 ($C_{24}H_{36}O$), 302.2582 ($C_{21}H_{34}O$), 299.2349 ($C_2H_{31}O$), 257.2003 ($C_{18}H_{25}O$), 243.1795 ($C_{17}H_{23}O$); $^1$H NMR: $\delta$ 0.40 (1H, *d*, *J* = 4.4 Hz, H-19 *exo*), 0.62 (1H, *d*, *J* = 4.0 Hz, H-19 *endo*), 0.87 (3H, *d*, *J* = 6.6 Hz, $H_3$-21), 0.91 (3H, *s*, $H_3$-30), 0.99 (3H, *d*, *J* = 6.2 Hz, $H_3$-28), 1.00 (3H, *s*, $H_3$-18), 1.10 (6H, *d*, *J* = 7.0 Hz, $H_3$-26, $H_3$-27), 2.62 (1H, *hept.*, *J* = 7.0 Hz, H-25).

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