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Pentacyclic triterpenes from *Euphorbia stygiana*

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Abstract

Two pentacyclic triterpenes, D-friedomadeir-14-en-3β-yl acetate and D:C-friedomadeir-7-en-3β-yl acetate, named madeiranyl acetate and isomadeiranyl acetate, respectively, were isolated from leaves of *Euphorbia stygiana*, together with the two known madeiranes, D-friedomadeir-14-en-3-one and D:C-friedomadeir-7-en-3-one, which were obtained from the stem bark. In addition, four known lupane and taraxerane-type triterpenes, namely lupenyl acetate, lupenone, taraxeryl acetate and taraxerone, were also isolated from the same source. Structures were elucidated by physical, chemical and spectroscopic methods (^{1}H NMR, ^{13}C NMR, IR and mass spectra) and by comparison with literature data, and in the case of D:C-friedomadeir-7-en-3β-yl acetate by X-ray analysis as well.

Keywords: *Euphorbia stygiana*; Euphorbiaceae; Pentacyclic triterpenes; Madeiranes; Lupanes; Taraxeranes

1. Introduction

Euphorbia stygiana Watson (Euphorbiaceae), a shrub endemic to the archipelago of Azores, is closely related to *Euphorbia mellifera* Ait., with the latter being found in the archipelago of Madeira and in two of the Canary islands. *E. stygiana* produces a latex which causes irritation of the skin and eyes during collection, and has also been reported to possess molluscicidal activity (Mendonça et al., 1993). However, no chemical investigation on this plant has been reported up to now. In this regard, the plant was screened for triterpenoids and four pentacyclic triterpenes were found with a madeirane skeleton: of these, two were new triterpenes, D-friedomadeir-14-en-3β-yl acetate and D:C-friedomadeir-7-en-3β-yl acetate, named madeiranyl acetate (**1a**) and isomadeiranyl acetate (**2a**), respectively, and the others were the two known triterpenes, D-friedomadeir-14-en-3-one (**1b**) and D:C-friedomadeir-7-en-3-one (**2b**), previously isolated from *E. mellifera* (Ferreira, 1990). In addition, four known pentacyclic triterpenes of the lupane and taraxerane-type skeleton were also isolated: lupenyl acetate, taraxeryl acetate, lupenone and taraxerone. The acetates were isolated from the leaves and the ketones from the stem bark.

2. Results and discussion

The acetone extracts from the air-dried stem bark and leaves of *E. stygiana* were individually partitioned between 85% aqueous MeOH and *n*-hexane. Each of the corresponding *n*-hexane soluble fractions were then saponified, with the non-saponifiable constituents being subjected to silica gel column chromatography using *n*-hexane–EtOAc gradients as eluants. Recrystallization of the resulting fractions yielded eight pentacyclic triterpenes: four acetates, madeiranyl acetate (**1a**), isomadeiranyl acetate (**2a**), lupenyl acetate and taraxeryl acetate, isolated from the leaves, and four ketones, madeiranone (**1b**), isomadeiranone (**2b**), lupenone and taraxerone, isolated from the stem bark. The acetates **1a** and **2a** are new compounds, whereas ketones **1b** and **2b** were previously reported in *E. mellifera*. The structures of the lupane and taraxerane-type triterpenes were established according to spectral data analysis and by comparison with published reported data (Lima, 2000).

The molecular formulae, $C_{32}H_{52}O_2$, of the acetates **1a** and **2a**, and $C_{30}H_{48}O$, of the ketones **1b** and **2b**,

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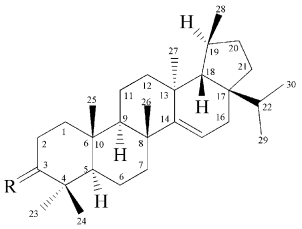
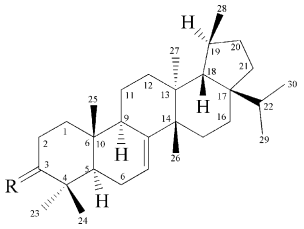


1a, R = α-H, β-OAc
1b, R = O



2a, R = α-H, β-OAc
2b, R = O

were deduced by EIMS (molecular ion at $m/z = 468$ and 424, respectively), elemental analysis and by analysis of the ^{13}C NMR spectroscopic data. The ^{13}C NMR spectra of the acetates (**1a** and **2a**) and of the ketones (**1b** and **2b**) showed 32 and 30 carbon signals, comprising, respectively, nine and eight methyls, nine methylenes, seven and six methines and seven quaternary carbons as indicated in DEPT experiments (Table 1); the assignments of the ^{13}C resonances were made by comparison with literature data (Ferreira, 1990; McLean et al., 1994). Analysis of the IR spectra revealed carbonyl bands for the ketones **1b** and **2b** (1700 cm^{-1}) and ester bands for the acetates **1a** and **2a** (1725 and 1237 cm^{-1}). The nature of the functional groups was confirmed in the ^{13}C NMR spectra (Table 1) by a signal at δ 217.63 (**1b**) and δ 217.03 (**2b**) for the ketones and by resonances at δ 81.00 and 81.09 (C-3), at δ 21.33 and 21.31 ($\underline{C}H_3COO$–) and at δ 171.00 and 170.96 ($CH_3\underline{C}OO$–), respectively, for the acetates **1a** and **2a**. In compounds **1a** and **2a**, the mass spectral fragments due to loss of acetic acid from the molecular ion also confirmed the presence of an acetyl moiety. The ^1H NMR spectra of the acetates (Table 2) showed the presence of a proton attached to C-3 with a large coupling constant (δ 4.46, *dd*, $J_{ae} = 5.9$ Hz, $J_{aa} = 10.1$ Hz for **1a**; δ 4.51, *dd*, $J_{ae} = 4.0$ Hz, $J_{aa} = 11.0$ Hz for **2a**) characteristic of an equatorial (β-) orientation of the acetyl moiety. The ^1H NMR spectra of the compounds **1a–b** and **2a–b** (Table 2) showed five singlets, attributed to tertiary methyl groups, and three doublets, attributed to a Me group located in the E-ring at C-19 (Ferreira, 1990) and to an isopropyl group located in the D/E-ring junction at C-17 (Ferreira, 1990); accordingly, the skeleton of these compounds differs from that of representatives of the hopane or lupane class. The unusual substitution pattern in the cyclopentane ring E for **2a** was established unambiguously by X-ray analysis (Fig. 1). The presence of an isopropyl group was also indicated by characteristic fragment ions peaks in the mass spectra, as e.g. the ion at m/z 161, for compounds **1a–b**, due to the loss of 43 mass units from the fragment ion peak at m/z 204.

The ^1H NMR spectra of **1a–b** (Table 2) also showed one olefinic proton (δ 5.41, *dd*, $J = 2.2$ and 7.9 Hz in **1a**; δ 5.44, *dd*, $J = 2.5$ and 8.0 Hz in **1b**) attributed to the proton at C-15. This assignment was based on the observed fragmentation patterns in the mass spectra of **1a–b**, typical of pentacyclic triterpenes with a C14–C15 double bond (Budzikiewicz et al., 1963). The ^{13}C NMR spectra (Table 1), with signals at δ 157.29 (C-14) and 118.20 (C-15) for **1a** and at δ 156.95 (C-14) and 118.43

Table 1
^{13}C NMR spectral data for **1a**, **1b**, **2a** and **2b** (75.47 MHz, TMS, $CDCl_3$)[a]

DEPT	C	1a	1b	C	2a	2b
CH_3	24	16.59	21.52	27	13.08	12.76
CH_3	25	15.36	14.70	24	15.82	21.57
CH_3		16.67	16.66		16.98	17.01
CH_3		18.99	18.99		17.33	17.35
CH_3		19.47	19.55	25	22.90	23.07
CH_3		24.51	24.51		24.13	24.27
CH_3		25.18	24.85	26	25.76	25.77
CH_3	23	27.96	26.04	23	27.51	24.51
CH_3	$\underline{C}H_3COO$–	21.33	–	$\underline{C}H_3COO$–	21.31	–
CH_2	11	17.12	17.06	11	16.77	16.94
CH_2	6	18.63	19.90		22.07	22.09
CH_2	2	23.43	34.15	6	23.90	24.51
CH_2		30.19	30.19	2	24.15	34.91
CH_2		32.25	32.14		28.36	28.45
CH_2		33.32	33.31		30.98	31.00
CH_2	1	37.35	38.34		35.17	35.13
CH_2		38.50	38.52		35.80	35.85
CH_2		41.53	40.95	1	36.58	38.33
CH	22	33.99[b]	34.00[b]	22	33.51[b]	33.53[b]
CH	19	34.36[b]	34.36[b]	19	35.06[b]	35.13[b]
CH	9	49.33	48.84	9	48.37	48.05
CH	5	55.49	55.70	5	50.33	51.93
CH	18	63.40	63.42	18	56.52	56.57
CH	3	81.00	–	3	81.09	–
CH	15	118.20	118.43	7	116.69	116.90
C	13	37.63	37.66	10	35.06	35.27
C	10	37.81	38.29	13	36.95[c]	36.98[c]
C	4	38.97	47.56	4	37.68	47.74
C	8	38.39	38.96	14	40.41[c]	40.57[c]
C	17	50.13	50.13	17	46.70	46.72
C	14	157.29	156.95	8	145.43	145.51
C	$CH_3\underline{C}OO$–	171.00	–	$CH_3\underline{C}OO$–	170.96	–
C	3	–	217.63	3	–	217.03

[a] δ in ppm.
[b] Can be interchanged within same column (Ferreira, 1990).
[c] Can be interchanged within same column (Ferreira, 1990).

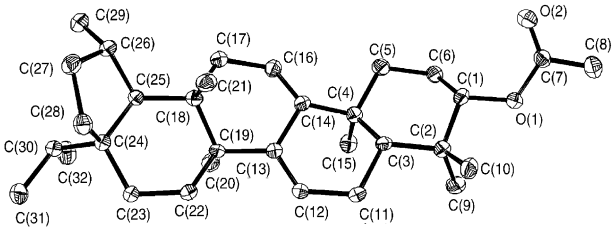


Fig. 1. Molecular structure of D:C-friedomadeir-7-en-3β-yl acetate (**2a**) obtained by X-ray analysis with atomic labeling.

Table 2
^{1}H NMR spectral data for **1a**, **1b**, **2a** and **2b** (300.13 MHz, TMS, $CDCl_3$)[a]

Position	1a	1b	2a	2b
Me-4α	0.85, 3H, *s*	1.07[b], 3H, *s*	0.85, 3H, *s*	1.04, 3H, *s*
Me-4β	0.87, 3H, *s*	1.08[b], 3H, *s*	0.93, 3H, *s*	1.11, 3H, *s*
Me-10β	0.93, 3H, *s*	1.07[b], 3H, *s*	0.77, 3H, *s*	1.00, 3H, *s*
Me-8β	1.02, 3H, *s*	1.06[b], 3H, *s*	–	–
Me-13α	0.94, 3H, *s*	0.94, 3H, *s*	0.92, 3H, *s*	0.94, 3H, *s*
Me-14β	–	–	0.95, 3H, *s*	0.95, 3H, *s*
Me-19β	1.04, 3H, *d* (6.8)	1.05, 3H, *d* (6.7)	1.07, 3H, *d* (7.3)	1.08, 3H, *d* (7.2)
Me-29 or Me-30	0.71, 3H, *d* (6.8)	0.72, 3H, *d* (6.8)	0.83, 3H, *d* (6.8)	0.83, 3H, *d* (6.8)
Me-30 or Me-29	0.77, 3H, *d* (6.8)	0.78, 3H, *d* (6.8)	0.94, 3H, *d* (6.8)	0.95, 3H, *d* (6.8)
H-3α	4.46, 1H, *dd* (5.9, 10.1)	–	4.51, 1H, *dd* (4.0, 11.0)	–
H-7	–	–	5.44, 1H, *m* ($w_{1/2}$ 11.0)	5.50, 1H, *m* ($w_{1/2}$ 11.0)
H-15	5.41, 1H, *dd* (2.2, 7.9)	5.44, 1H, *dd* (2.5, 8.0)	–	–
AcO-3β	2.04, 3H, *s*	–	2.05, 3H, *s*	–

[a] δ in ppm and J (parentheses) in Hz.
[b] Can be interchanged within same column (Ferreira, 1990).

(C-15) for **1b**, corresponding to the two sp^2 carbons, confirmed the location of this double bond (Sakurai et al., 1987). Compounds **1a** and **1b** were thus identified as D-friedomadeir-14-en-3β-yl acetate and D-friedomadeir-14-en-3-one, respectively.

The ^{1}H NMR spectra of **2a–b** (Table 2) also showed one olefinic proton (δ 5.44, *m*, $W_{1/2}$ = 11.0 Hz for **2a**; δ 5.50, *m*, $W_{1/2}$ = 11.0 Hz for **2b**) attributed to the proton at C-7; this assignment was established by analysis of the MS, ^{13}C NMR and X-ray crystal data and from the close analogy with the ^{1}H NMR spectral data of compounds with C-7 unsaturation, as explained below. The fragmentation patterns in the mass spectra of **2a–b**, were consistent with that observed for pentacyclic triterpenes methylated at C-13 and C-14 with $\Delta^{7,8}$, $\Delta^{8,9}$ or $\Delta^{9(11)}$ unsaturation (Budzikiewicz et al., 1963; Ogunkoya, 1981). The presence of a trisubstituted double bond C7-C8 was confirmed in the ^{13}C NMR spectra (Table 1) by the resonances at δ 116.69 (C-7) and 145.43 (C-8) for **2a** and at δ 116.90 (C-7) and 145.51 (C-8) for **2b** (Knight and Res, 1974), and from the shorter bond length (1.32 Å). The signals of Me-4α, Me-4β and Me-10β in the ^{1}H NMR spectra (Table 2) are also in good agreement with those of triterpenoids with C6-C7 double bond (Akihisa et al., 1986).

Compounds **2a** and **2b** were thus identified as D:C-friedomadeir-7-en-3β-yl acetate and D:C-friedomadeir-7-en-3-one, respectively.

On reduction with $NaBH_4$, the ketones **1b** and **2b** were converted into the corresponding alcohols identical with authentic samples in co-GC. Moreover, on acetylation with Ac_2O/pyridine, the alcohols were also converted into the corresponding acetates, these being identical with the natural acetates **1a** and **2a** in mmp and co-GC. Thus, this proves the structural relationship between the ketones **1b** and **2b** and the acetates **1a** and **2a**, respectively, and the chemotaxonomic similarities between both species of *Euphorbia*.

3. Experimental

3.1. General experimental procedures

Melting points (uncorr.) were determined on a Electrothermal IA 8103 apparatus. Optical rotations were measured in $CHCl_3$ with a Perkin-Elmer 243S polarimeter. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer with KBr discs. ^{1}H NMR (300.13 MHz) and ^{13}C NMR (75.47 MHz) spectra were measured on a Bruker AMX-300 spectrometer with TMS as internal standard and $CDCl_3$ as solvent. The number of attached protons for ^{13}C signals was determined using the DEPT pulse sequence. EIMS (70 eV) was carried out on a VG Auto Spec Q instrument. GC analysis was carried out with a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector (column, OV-101, 15 m × 0.33 mm × 0.18 μm; carrier gas, N_2 at 30 ml min^{-1}; temp. program, 180–240 °C at 5 C min^{-1}; injection and detection temp., 300 °C). Silica gel 60 (70–230 mesh, Merck) was used for column chromatography.

3.2. Plant material

The plant material (leaves and stem bark) of *E. stygiana* Watson was collected in Pico island, Açores, Portugal, in August 1994, and identified by members of the Department of Biology, University of Azores, where a voucher specimen is stored.

3.3. Extraction

The air-dried and finely powdered plant material [leaves (I) and stem bark (II), 600 g each] of *E. stygiana* were individually extracted with Me_2CO at room temp. for 7 days. Each extract was filtered on a Büchner funnel and conc. in vacuo. The extracts (I–81 g; II–97 g) were then individually suspended in 85% aq. MeOH

and partitioned with *n*-hexane to give, following evaporation in vacuo, residues of 19 g for I and 20 g for II.

3.4. Saponification

Solutions of 10% KOH in MeOH (100 ml) were individually added to the total *n*-hexane extracts of I and II. After refluxing until complete dissolution, the resulting mixtures were left at room temp. for 24 h. After concentration of each of the MeOH solubles in vacuo, the residues were suspended in H_2O (100 ml) and extracted with Et_2O (6 × 50 ml). The combined Et_2O extracts containing the non-saponifiable part were dried (Na_2SO_4) and evaporated, yielding residues of ~10 g for I and II, respectively.

3.5. Isolation

3.5.1. Leaves

The non-saponifiable part of the *n*-hexane extract of the leaves (10 g) was subjected to CC on silica gel (300 g) using a gradient of *n*-hexane–EtOAc, with the 46 eluted fractions (100 ml each) being combined to give seven fractions (A–G).

Fraction B (nos 12–15; 620 mg; *n*-hexane–EtOAc, 98:2) was dissolved in hot Me_2CO. On cooling, the ppt. (20 mg) was removed by filtration and was identified as taraxeryl acetate. The mother liquor was partially conc. and cooled, yielding a ppt. (60 mg) with two types of crystals, one as a white powder and the other as white granular crystals, which were separated by hand into individual compounds: the powdered product (20 mg) was recrystallized twice from Me_2CO to give madeiranyl acetate (**1a**) (11 mg) and the granular product (40 mg) was recrystallized from Me_2CO to give isomadeiranyl acetate (**2a**) (29 mg). The residue of the mother liquor was recrystallized twice from Me_2CO/MeOH. The residue from the mother liquor of the second recrystallization was dissolved in hot MeOH and decolorized with activated carbon to give lupenyl acetate (10 mg).

3.5.2. Stem bark

The non-saponifiable part (10 g) of the stem bark extract was separated by CC on silica gel (300 g) with mixtures of *n*-hexane–EtOAc of increasing polarity. The 56 eluted fractions of 100 ml were combined in eight fractions (A–H).

Fraction B (no. 19; 120 mg; *n*-hexane–EtOAc, 99:1) was dissolved in hot Me_2CO. On cooling, a mixture (22 mg) crystallized showing two components in GC, which were purified from fraction C (taraxerone) and from fraction E (compound **1b**). The mother liquor was allowed to stand at 0 °C yielding isomadeiranone (**2b**) (30 mg).

Fraction C (no. 20; 140 mg; *n*-hexane–EtOAc, 99:1) was dissolved in hot Me_2CO. On cooling, the ppt. was removed by filtration to give taraxerone (20 mg).

Fraction D (no. 21; 430 mg; *n*-hexane–EtOAc, 99:1) was dissolved in hot Me_2CO. On cooling, a mixture (163 mg) crystallized showing the same components reported for fraction B (taraxerone and compound **1b**). The mother liquor was allowed to stand at 0 °C yielding a mixture (50 mg) of two compounds: compound **1b** and lupenone. The residue (217 mg) of the mother liquor was recrystallized twice from Me_2CO/CH_2Cl_2 to give lupenone (30 mg).

Fraction E (nos 23–31; 550 mg; *n*-hexane–EtOAc, 98:2) was dissolved in hot Me_2CO. On cooling, the ppt. (60 mg) was removed by filtration, giving ca. 70% of madeiranone (**1b**) by GC analysis. The filtrate yielded another ppt. (40 mg; ca. 95% of **1b**) that was recrystallized from Me_2CO to give pure **1b** (22 mg).

3.6. D-Friedomadeir-14-en-3β-yl acetate (*1a*)

White powder, mp 220–221 °C, $[\alpha]_D$ +23.4° (*c* 0.6, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 2950, 2875, 1725, 1460, 1375, 1237, 1163, 1140, 1100, 1030, 1000, 950, 925, 900, 850, 800. For ^{13}C and ^{1}H NMR spectral data, see Tables 1 and 2. EIMS *m/z* (rel. int.): 468 (15), 453 (14), 425 (7), 393 (4), 365 (5), 344 (32), 329 (14), 284 (4), 269 (11), 257 (9), 245 (3), 231 (6), 229 (7), 218 (29), 204 (100), 175 (19), 161 (41), 159 (12), 149 (23), 148 (16), 147 (19), 145 (11), 135 (40), 133 (28), 131 (8), 123 (29), 121 (30), 119 (23), 109 (25), 107 (32), 105 (18), 95 (33), 93 (19), 91 (9), 85 (4), 83 (10), 81 (30), 69 (32), 55 (22). Anal. (Found: C, 81.72; H, 11.04. $C_{32}H_{52}O_2$ requires: C, 81.99; H, 11.18%).

3.7. D-Friedomadeir-14-en-3-one (*1b*)

White powder, mp 176–178 °C, $[\alpha]_D$ +27° (*c* 0.52, $CHCl_3$) [lit. (Ferreira, 1990): mp 177–179°C, $[\alpha]_D$ +27.5°]. IR (KBr) ν_{max} cm^{-1}: 2950, 2850, 1700, 1455, 1385, 1375, 1000. For ^{13}C and ^{1}H NMR spectral data, see Tables 1 and 2. EIMS *m/z* (rel. int.): 424 (38), 409 (28), 381 (16), 300 (73), 285 (38), 271 (7), 257 (12), 243 (7), 232 (8), 204 (100), 189 (24), 175 (22), 161 (63), 159 (13), 149 (30), 147 (24), 145 (15), 135 (24), 133 (49), 131 (11), 123 (39), 121 (36), 119 (32), 109 (38), 107 (45), 105 (32), 95 (46), 93 (28), 91 (20), 83 (91), 81 (46), 69 (33), 55 (35). Anal. (Found: C, 84.78; H, 11.31. Calc. for $C_{30}H_{48}O$: C, 84.84; H, 11.39%).

3.8. D:C-Friedomadeir-7-en-3β-yl acetate (*2a*)[1]

White granular crystals, mp 213–214 °C, $[\alpha]_D$ −61.5° (*c* 0.75, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 2950, 2875, 1725,

[1] *Crystal Data*. **2a**: $C_{32}H_{52}O_2$, $M = 468.7$, monoclinic, $a = 9.621(7)$, $b = 9.457(7)$, $c = 15.780(12)$ Å, $\beta = 107.63(2)°$, $V = 1368$ Å^3, space group $P2_1$, $Z = 2$, $D_c = 1.14$ g cm^{-3}, $F(000) = 520$. Data were measured on a Siemens SMART 1K diffractometer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

1460, 1385, 1375, 1237, 1163, 1110, 1025, 1010, 990, 970, 900, 865, 855, 825, 815. For ^{13}C and ^{1}H NMR spectral data, see Tables 1 and 2. EIMS *m/z* (rel. int.): 468 (29), 453 (45), 425 (49), 408 (2), 393 (14), 365 (27), 329 (13), 316 (5), 315 (0.5), 301 (58), 289 (10), 281 (2), 267 (2), 262 (40), 257 (17), 255 (16), 243 (18), 241 (33), 229 (39), 221 (3), 206 (38), 205 (87), 204 (36), 203 (22), 202 (24), 189 (14), 187 (22), 173 (19), 171 (8), 169 (3), 163 (23), 161 (22), 159 (24), 157 (8), 149 (41), 147 (24), 145 (19), 135 (63), 133 (34), 131 (15), 123 (52), 122 (14), 121 (46), 119 (36), 117 (7), 109 (69), 108 (18), 107 (100), 105 (27), 95 (67), 93 (32), 81 (54), 69 (49), 55 (38). Anal. (Found: C, 81.55; H, 11.09. $C_{32}H_{52}O_2$ requires: C, 81.99; H, 11.18%).

3.9. D:C-Friedomadeir-7-en-3-one (**2b**)

White powder, mp 202–203 °C, $[\alpha]_D$ −21° (*c* 0.6, $CHCl_3$) [lit. (Ferreira, 1990): mp 201.5–202.8°C, $[\alpha]_D$ −19.8°]. IR (KBr) ν_{max} cm^{-1}: 2950, 2875, 1700, 1462, 1385, 1365. For ^{13}C and ^{1}H NMR spectral data, see Tables 1 and 2. EIMS *m/z* (rel. int.): 424 (43), 409 (42), 381 (87), 285 (36), 271 (29), 257 (66), 245 (39), 218 (95), 205 (98), 189 (34), 187 (21), 177 (25), 175 (33), 173 (25), 163 (36), 161 (39), 159 (29), 151 (28), 149 (51), 147 (44), 145 (31), 135 (52), 133 (51), 131 (27), 123 (72), 121 (65), 119 (52), 117 (18), 109 (90), 107 (100), 105 (50), 95 (94), 93 (54), 91 (40), 84 (58), 69 (86), 55 (83). Anal. (Found: C, 84.74; H, 11.54. Calc. for $C_{30}H_{48}O$: C, 84.84; H, 11.39%).

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