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TRITERPENOID SAPOGENOLS FROM THE LEAVES OF *CAREYA ARBOREA*: STRUCTURE OF CAREYAGENOLIDE

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Key Word Index—*Careya arborea*; Lecythidaceae; careyagenolide; maslinic acid; 2α-hydroxy ursolic acid.

Abstract—The acid hydrolysate of the ethanol extract of *Careya arborea* leaves afforded a new triterpenoid lactone designated careyagenolide along with maslinic acid and 2α-hydroxy ursolic acid. The structure of careyagenolide has been established as 2α, 3β-dihydroxytaraxastan-28, 20β-olide by a variety of spectroscopic evidence, chemical transformations and correlation with ψ-taraxasterol.

INTRODUCTION

The fruits and seeds of *Careya arborea* have been reported to contain cardiac glycosides [1, 2]. The phytotoxic properties of the plant against certain forest weeds have been studied [3]. A number of sterols and triterpenoid sapogenols have been isolated from the leaves and seeds of the plant [4–8]. The present paper describes the isolation from the leaves and structure elucidation of a new triterpenoid lactone, careyagenolide, along with the isolation and characterization of maslinic acid and 2α-hydroxy ursolic acid.

RESULTS AND DISCUSSION

Extensive Si gel CC followed by prep. TLC of the petrol extract of the acid hydrolysate of the ethanol extract of *C. arborea* leaves yielded a new triterpenoid lactone (**1**) and a mixture of triterpenoid acids (**2** and **3**). The acids **2** and **3** could be efficiently separated by preparation of their methyl esters and subsequent fractional crystallizations.

The methyl ester (**4**) of **2** exhibited IR absorptions attributable to ester carbonyl and hydroxyl functions. The mass spectrum of the methyl ester (**4**) showed a molecular ion peak at *m/z* 468 and RDA-fragment ion peaks characteristic of a Δ^{12}-oleanene or ursene skeleton [9]. The ^{1}H NMR spectrum suggested the presence of two vicinal hydroxyl groups. The methyl ester (**4**) and the acid (**2**) obtained by saponification of **4** with 20% ethanolic potassium hydroxide were finally identified as methyl maslinate and maslinic acid respectively by comparison with authentic samples (mp, mmp, IR and ^{1}H NMR).

The methyl ester (**5**) of **3** showed similar spectral characteristics to those of **4** and on saponification it yielded the acid **3** which was eventually characterized as 2α-hydroxy ursolic acid by comparison of its IR, ^{1}H NMR and mass spectrum with those of an authentic sample.

Compound **1**, $C_{30}H_{48}O_4$ (M^+ at *m/z* 472), mp 299° (dec.) was obtained as a minor constituent. The molecular formula and positive Lieberman–Burchard test indicated it to be a triterpene. The IR spectrum showed strong absorption bands at 3500 (*br*) and 1720 cm^{-1} assignable to hydroxyl and carbonyl functions respectively. The presence of two hydroxyl groups in **1** was ascertained by preparation of its diacetate (**6**), $C_{34}H_{52}O_6$ (M^+ at *m/z* 556). Compound **1** did not show the characteristics of an acid or an α-diketone nor did the ^{1}H NMR spectrum of **1** indicate the presence of a keto-methylene group. As a consequence, the carbonyl absorption band in the IR spectrum of **1** was ascribed to a lactone carbonyl group. Moreover, the absorption band at 1720 cm^{-1} strongly suggested **1** to have a six-membered lactone ring. The skeleton, the positions of the hydroxyl groups and the carbon atoms involved in the formation of the lactone ring were revealed by the following chemical and spectroscopic evidence.

The mass spectral fragmentation pattern of **1** was indicative of a saturated pentacyclic triterpene. The peak at *m/z* 223 may be attributed to the fragment ion **14** involving rings A/B and the two hydroxyl groups being present in this part. The presence of a hydroxyl group at C-3 was assumed from biogenetic considerations and was subsequently ascertained by chemical correlation (see below). Moreover, the vicinal disposition of the two hydroxyl groups was proved by preparation of the acetonide (**7**). The ^{1}H NMR spectrum (270 MHz) of **6** displayed two downfield signals at δ 4.74 as a doublet (J = 10 Hz) and 5.12 as a hextet (J = 10, 10 and 5 Hz) which demonstrated 2α,

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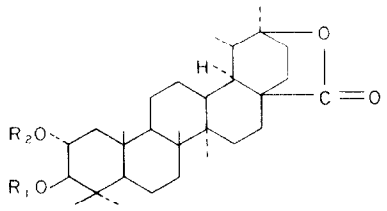

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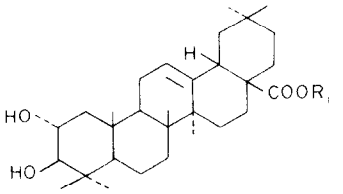
6 $R_1 = R_2 = Ac$



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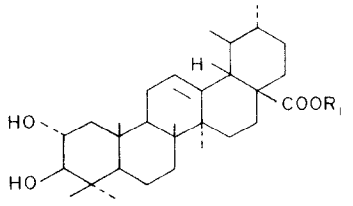

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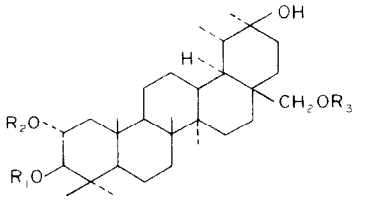

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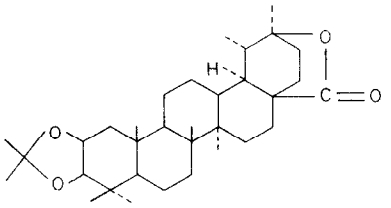
9 $R_1 = R_2 = R_3 = Ac$



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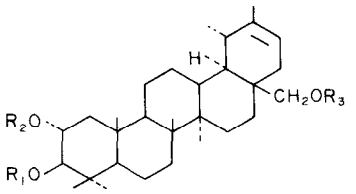
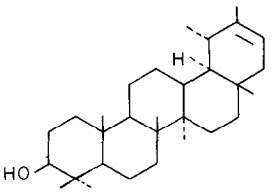
3β orientations of the two hydroxyl groups [10]. Furthermore, the ^{1}H NMR spectrum exhibited signals ascribed to six tertiary and one secondary methyl groups. The methyl singlet at δ 1.32 in the ^{1}H NMR spectrum of **6** shifted upfield in the ^{1}H NMR spectrum of the tetraol (**8**) obtained on lithium aluminium hydride reduction of **1** in refluxing dioxane for 16 hr (mild conditions were unsuccessful). The tetraol (**8**) on acetylation with acetic anhydride and pyridine furnished an amorphous triacetate (**9**) which showed a hydroxyl band at 3300 cm^{-1} in its IR spectrum. The tertiary nature of this fourth hydroxyl group was confirmed from the ^{1}H NMR spectrum of **9** (no signal attributable to a proton geminal to a hydroxyl) and also by the fact that **9** could not be oxidized to a ketone. Consequently, the attachment of the tertiary hydroxyl group in **9** and hence of the lactonic function in **1** to one of the secondary methyls in ring E of ursane or ψ-taraxastane skeleton was indicated. Considering the lactonic ring to be six-membered, the involvement of either C-27 and C-19 or C-28 and C-20 in the formation of the lactone ring would be the two feasible propositions. Compound **9** on dehydration with $POCl_3$ in pyridine yielded **10** as the major product, the ^{1}H NMR spectrum of which showed a triplet (1 H) at δ 5.22 and a singlet (3 H) at 1.64 assigned to a vinylic proton and vinylic methyl group respectively. It follows, therefore, that only **1** with the lactone ring involving C-28 and C-20 could yield on lithium aluminium hydride reduction and acetylation followed by dehydration a trisubstituted double bond as in **10**.

The configurations of H-18 and H-19 were also revealed by the ^{1}H NMR spectrum of **6**. The spectrum showed a quartet (1 H) at δ 2.11 (J = 12.5 and 4.5 Hz) assigned to H-18 by comparison of the ^{1}H NMR spectra of a series of pentacyclic triterpenes [11, 12]. The larger coupling constant of 12.5 Hz indicated not only the *trans*-diaxial relationship between H-18 and H-13 but also the conformational rigidity of the E ring [13, 14]. Moreover, the smaller coupling constant of 4.5 Hz suggested the dihedral angle between H-18 and H-19 to be of *ca* 60 or 120°. Drieding model inspection of **6** revealed the angles to be of *ca* 0 and 110° for the α- and β-orientations of the H-19 respectively. Considerable distortion would have to be introduced into ring E to produce an angle of 60° and it was concluded, therefore, that H-19 in **1** has a β-configuration. Finally, the stereochemistry of the skeleton of **1** was confirmed by its chemical correlation with ψ-taraxasterol (**11**). Compound **10** obtained from **1** as described above on refluxing with Li-$(CH_2NH_2)_2$ [15, 16] for 25 min in a nitrogen atmosphere yielded a major product, mp 190–193° which was found identical in all respects (mp, mmp, TLC, IR, MS) with an authentic sample of ψ-taraxasterol.

All the foregoing evidence led to the establishment of the structure of careyagenolide as 2α, 3β-dihydroxytaraxastan-28, 20β-olide (**1**).



10 $R_1 = R_2 = R_3 = Ac$



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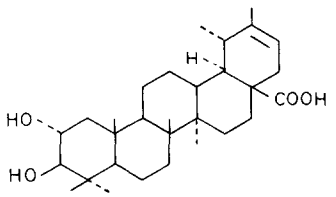

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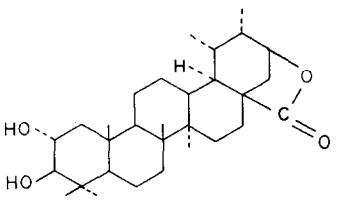

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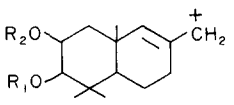

14 $R_1 = R_2 = H$

15 $R_1 = R_2 = Ac$

In order to determine whether lactonization of maslinic acid (**2**) or 2α-hydroxy ursolic acid (**3**) which are present in the plant could lead to careyagenolide (**1**) under conditions of acid hydrolysis a mixture (50 mg) of **2** and **3** was refluxed for 6 hr with 6% ethanolic hydrochloric acid but the starting material was recovered unchanged. This is quite expected because of the fact that the equatorial orientations of the H-18 in acids **2** and **3** are kinetically unfavourable for this sort of rearrangement process [17].

It is noteworthy that **1** did not yield any product on saponification with 10% ethanolic potassium hydroxide for 8 hr at 100°. However, on refluxing with 40% potassium hydroxide in diethylene glycol for 8 hr it afforded an acid mixture as evident from TLC (R_f value very similar to maslinic or 2α-hydroxy ursolic acid). These acids undergo lactonization readily during purification giving rise to a mixture of five-membered lactones (IR absorption band at 1752 cm^{-1}) from which the major product **13** could be obtained by fractional crystallization as needles, mp 232–234°. Its ^1H NMR spectrum displayed signals at δ 4.08 (*ddd*, $J = 8$, 8 and 2.5 Hz) assigned to H-21 and at 2.23 (*dd*, $J = 11$ and 11 Hz) ascribed to H-18 with an α-(axial)-configuration which revealed that the skeleton was unchanged even after drastic conditions of saponification. It may reasonably be presumed that the acid **12** on spontaneous lactonization yields **13**.

EXPERIMENTAL

Mps are uncorr. ^1H NMR spectra were recorded on 100 and 270 MHz instruments in $CDCl_3$ soln with TMS as int. standard. MS were determined by a direct inlet system with 70 eV ionization. IR spectra were run as KBr pellets.

Isolation of the triterpenoid sapogenols. Finely ground leaves of *C. arborea* (3 kg) were defatted with petrol and extracted successively with $CHCl_3$ and EtOH. The EtOH extract (40 g) was hydrolysed with 6% aq. HCl for 6 hr at 100°. The dried acid free hydrolysate was dissolved in $CHCl_3$–MeOH and adsorbed on paper pulp, which on exhaustive extraction with petrol gave a residue (5 g) after evaporation of the solvent. The residue was chromatographed on a Si gel column to give **1** and a mixture of **2** and **3**. Compounds **2** and **3** were separated by esterification with an ethereal soln of CH_2N_2 followed by fractional crystallization.

Methyl maslinate (**4**). Compound **4** crystallized from MeOH as needles, mp 227–228°; IR ν_{max}^{KBr} cm^{-1}: 1725, 3350; MS *m/z*: 486 $[M]^+$, 468 $[M-H_2O]^+$, 450 $[M-2H_2O]^+$, 262 [retro Diels–Alder fragment **a**]$^+$ (100%), 203 [**a** – COOMe]$^+$; ^1H NMR ($CDCl_3$): δ 0.72 (3 H, *s*), 0.90 (3 H, *s*), 0.91 (3 H, *s*), 0.92 (3 H, *s*), 1.08 (3 H, *s*), 1.14 (3 H, *s*), 3.05 (*d*, $J = 10$ Hz, H-3), 3.60 (3 H, *s*), 3.65 (*m*, H-2), 5.24 (1 H, *m*).

Maslinic acid (**2**). Compound **4** on saponification with 20% KOH–EtOH for 6 hr furnished an acid, mp 297–280°; IR ν_{max}^{KBr} cm^{-1}: 1690, 3340; MS *m/z*: 472 $[M]^+$ mp, mmp, IR, MS and ^1H NMR were identical with those of an authentic sample.

Methyl 2α-hydroxy ursolate (**5**). Crystallized from MeOH as needles, mp 211–213°; IR ν_{max}^{KBr} cm^{-1}: 1725, 3335; MS *m/z*: 486 $[M]^+$, 468 $[M-H_2O]^+$, 450 $[M-2H_2O]^+$, 262 [retro Diels–Alder fragment **a**]$^+$ (100%), 203 [**a**–COOMe]$^+$; ^1H NMR ($CDCl_3$): δ 0.74 (3 H, *s*), 0.82 (3 H, *s*), 0.92 (6 H, *d*, $J = 7$ Hz), 0.99 (3 H, *s*), 1.03 (3 H, *s*), 1.08 (3 H, *s*), 2.98 (*d*, $J = 9$ Hz, H-3), 3.60 (3 H, *s*), 3.65 (*m*, H-2), 5.25 (1 H, *m*).

2α-Hydroxy ursolic acid (**3**). Compound **5** on hydrolysis with 20% ethanolic KOH for 6 hr, afforded an acid, mp 244–246° (dec.); IR ν_{max}^{KBr} cm^{-1}: 1697, 3410; MS *m/z*: 472 [M]$^+$.

Careyagenolide (**1**). Compound **1** was crystallized repeatedly from MeOH to give plates, mp 299° (dec.); IR ν_{max}^{KBr} cm^{-1}: 3500, 1720, 1230, 1045; MS *m/z* (rel. int.): 472 [M]$^+$ (6), 454 [M−H_2O]$^+$ (3), 436 [M−2H_2O]$^+$ (8), 426 (1.5), 421 [M−2H_2O−Me]$^+$ (4), 411 (9), 393 (2.5), 355 (2.5), 303 (2.5), 261 (7.5), 235 (21), 223 [**14**]$^+$ (6.5), 219 (21), 205 [**14**−H_2O]$^+$ (39), 189 (51), 187 [**14**−2H_2O]$^+$ (50). (Found: C, 76.20; H, 10.21. $C_{30}H_{48}O_4$ requires: C, 76.23; H, 10.24%.)

Careyagenolide diacetate (**6**). Compound **1** (6 mg) furnished the diacetate (**6**) with Ac_2O (0.5 ml) and pyridine (0.5 ml) at room temp. for 12 hr. It crystallized from MeOH as $C_{34}H_{52}O_6$·2MeOH, mp 306–308°; IR ν_{max}^{KBr} cm^{-1}: 1730, 1240, 1030; ^{1}H NMR ($CDCl_3$): δ 0.88 (3 H, *s*), 0.89 (3 H, *s*), 0.90 (3 H, *s*), 0.97 (3 H, *s*), 0.98 (3 H, *s*), 0.99 (3 H, *d*, *J*=7 Hz), 1.32 (3 H, *s*), 1.98 (*s*, -OCOCH_3), 2.05 (*s*, -OCOCH_3), 2.11 (*dd*, *J*=12.5 and 4.5 Hz, H-18), 4.74 (*d*, *J*=10 Hz, H-3), 5.12 (*ddd*, *J*=10, 10 and 4.5 Hz, H-2); MS *m/z* (rel. int.): 556 [M]$^+$ (18), 496 [M−AcOH]$^+$ (3), 481 [M−AcOH−Me]$^+$ (16), 454 [M−AcOH−C_2H_2O]$^+$ (75), 436 [M−2AcOH]$^+$ (77), 421 [M−2AcOH−Me]$^+$ (24), 411 (7), 393 (15), 261 (10), 247 [**15**−AcOH]$^+$ (8), 234 (39), 219 (20), 203 (39), 187 [**15**−AcOH]$^+$ (65), 119 (58), 55 (100). (Found: C, 69.61; H, 9.70. $C_{34}H_{52}O_6$·2MeOH requires: C, 69.64; H, 9.74%.)

Isopropylidene derivatives of **1** (**7**). Compound **1** (3 mg) was treated for 24 hr at room temp. with 1 ml of reagent (50 ml Me_2CO, 1 ml Et_2O, and 0.1 ml conc. H_2SO_4). Excess $BaCO_3$ was added and the mixture stirred for 4 hr, evaporation of the filtrate, gave an amorphous substance (**7**), IR ν_{max}^{KBr} cm^{-1}: 1720, 1040; MS *m/z*: 512 [M]$^+$. (Found: C, 77.25; H, 10.20. $C_{33}H_{52}O_4$ requires: C, 77.30; H, 10.22%.)

Reduction of **1** *by* $LiAlH_4$. (a) Compound **1** (8 mg) was refluxed with $LiAlH_4$ (30 mg) in dry THF (4 ml) for 8 hr. After cautious addition of H_2O (5 ml) and neutralizing with dil. H_2SO_4, the mixture was extracted with Et_2O to give unreacted **1** (7.5 mg), mp 299° (dec.).

(b) Compound **1** (40 mg) was heated in refluxing dioxane (10 ml) with $LiAlH_4$ (75 mg) for 15 hr and worked-up in the usual way to give a tetraol (**8**, 32 mg) as needles from MeOH, mp 246–248°; IR ν_{max}^{KBr} cm^{-1}: 3500 (*br*), 1040; ^{1}H NMR ($CDCl_3$): δ 0.82 (3 H, *s*), 0.92 (3 H, *s*), 0.98 (3 H, *s*), 1.02 (3 H, *d*, *J*=7 Hz), 1.07 (3 H, *s*), 1.13 (3 H, *s*), 1.27 (3 H, *s*), 3.02 (1 H, *d*, *J*=10 Hz), 3.70 (1 H, *m*), 3.86 (2 H, *br s*) MS *m/z*: 476 [M]$^+$. (Found: C, 75.53; H, 10.93. $C_{30}H_{52}O_4$ requires: C, 75.58; H, 10.99%.)

Acetate of **8** (**9**). Compound **8** (26 mg) was treated with Ac_2O (1 ml) in pyridine (1 ml) at room temp. overnight and worked-up in the usual way. The product could not be crystallized from any solvent and was an amorphous solid (**9**, 25 mg), IR ν_{max}^{KBr} cm^{-1}: 3400, 1730 (*br*), 1240, 1030; ^{1}H NMR ($CDCl_3$): δ 0.89 (3 H, *s*), 0.95 (3 H, *d*, *J*=7 Hz), 0.99 (3 H, *s*), 1.06 (3 H, *s*), 1.11 (3 H, *s*), 1.26 (6 H, each *s*), 1.98 (*s*, -OCOMe), 2.07 (each *s*, -OCOMe×2), 4.26 (1 H, *d*, *J*=12 Hz, H-28), 4.46 (1 H, *d*, *J*=12 Hz, H-28), 4.74 (*d*, *J*=10 Hz, H-3), 5.12 (*ddd*, *J*=10, 10 and 4.5 Hz, H-2); MS *m/z* (rel. int.): 602 [M]$^+$ (0.3), 584 [M−H_2O]$^+$ (2), 542 [M−AcOH]$^+$ (18), 524 [M−AcOH−H_2O]$^+$ (5.4), 511 (3), 482 [M−2AcOH]$^+$ (2), 472 (2.5), 467 [M−2AcOH−Me]$^+$ (2.5), 464 [M−2AcOH−H_2O]$^+$ (2), 449 [M−AcOH−Me−H_2O]$^+$ (1.5), 440 (2.5), 422 (12.5), 411 (3.5), 404 (3), 391 (2.3), 347 (6), 323 (3.7), 307 (1.5), 262 (3.4), 219 (15.5), 203 (28.5), 189 (47), 119 (74), 87 (100). (Found: C, 75.52; H, 9.68. $C_{36}H_{58}O_7$ requires: C, 75.58; H, 9.70%.)

Dehydration of **9** *by* $POCl_3$. Compound **9** (18 mg) in pyridine (1 ml) was heated at 100° with $POCl_3$ (1 ml) for 3 hr. The soln was cooled and poured into ice and extracted with Et_2O to yield a crude product. TLC showed the existence of a major product in the reaction mixture. The major product, an acetoxy olefin, was separated by prep. TLC but could not be crystallized from any solvent and was an amorphous substance (**10**, 12.5 mg); IR ν_{max}^{KBr} cm^{-1}: 1730, 1240; ^{1}H NMR ($CDCl_3$): δ 0.90 (3 H, *s*), 0.94 (3 H, *d*, *J*=7 Hz), 0.99 (3 H, *s*), 1.04 (3 H, *s*), 1.24 (3 H, *s*), 1.41 (3 H, *s*), 1.64 (*s*, =C-Me), 1.99 (*s*, -OCOMe), 2.02 (each *s*, -OCOMe×2), 3.98 (1 H, *d*, *J*=12 Hz, H-28), 4.22 (1 H, *d*, *J*=12 Hz, H-28), 4.74 (*d*, *J*=10 Hz, H-3), 5.12 (*ddd*, *J*=10, 10 and 4.5 Hz), 5.22 (1 H, *m*); MS *m/z*: 584 [M]$^+$, 542 [M−C_2H_2O]$^+$, 524 [M−AcOH]$^+$, 509 [M−AcOH−Me]$^+$, 494 [M−AcOH−2Me]$^+$, 485, 482 [M−AcOH−C_2H_2O]$^+$, 467 [M−AcOH−C_2H_2O−Me]$^+$, 464 [M−2AcOH]$^+$, 449 [M−2AcOH−Me]$^+$, 440, 422, 404, 391. (Found: C, 73.89; H, 9.61. $C_{36}H_{56}O_6$ requires: C, 73.93; H, 9.65%.)

Saponification of **1**. (a) Compound **1** (5 mg) was refluxed with 10% KOH in MeOH (4 ml) and C_6H_6 (1 ml) for 8 hr. The product (4.5 mg), mp 299° (dec.) was identified as unchanged **1**.

(b) Compound **1** (10 mg) was refluxed with 40% KOH in diethylene glycol (3 ml) and the mixture monitored frequently by TLC to observe the progress of the reaction. After 2 hr, a spot in the vicinity of maslinic or 2α-hydroxy ursolic acid (R_f: 0.30; solvent system: C_6H_6–$CHCl_3$–MeOH, 6:3:1) appeared and became gradually more intense with the progress of time. After 8 hr when the reaction seemed to be complete, the mixture was diluted with H_2O and neutralized with dil. HCl and finally extracted with $CHCl_3$. TLC showed the complete conversion to another product of higher R_f value (R_f: 0.34; solvent system: C_6H_6–$CHCl_3$–MeOH, 6:3:1). The product was purified by prep. TLC (Si gel) and crystallized from MeOH to give needles (**13**, 4.5 mg), mp 232–234°; IR ν_{max}^{KBr} cm^{-1}: 3500, 1752, 1035; MS *m/z* (rel. int.): 472 [M]$^+$ (0.5), 454 [M−H_2O]$^+$ (2.3), 436 [M−2H_2O]$^+$ (0.5), 426 [M−COOH−H]$^+$ (2.2), 421 [M−2H_2O−Me]$^+$ (0.5), 411 (0.6), 408 (1.4), 393 (0.6), 263 (2.2), 223 [**14**]$^+$ (4.5), 205 [**14**−H_2O]$^+$ (10), 189 (9), 187 [**14**−2H_2O]$^+$ (7), 119 (37), 44 (100); ^{1}H NMR ($CDCl_3$): δ 0.81 (3 H, *s*), 0.90 (3 H, *s*), 0.97 (6 H, *s*), 1.38 (3 H, *s*), 1.45 (3 H, *s*), 2.23 (1 H, *dd*, *J*=11 and 11 Hz), 2.98 (*d*, *J*=10 Hz, H-3), 3.72 (*ddd*, *J*=10, 10 and 4.5 Hz), 4.08 (*ddd*, *J*=8, 8 and 2.5 Hz). (Found: C, 76.21; H, 10.22. $C_{30}H_{48}O_4$ requires: C, 76.23; H, 10.24%.)

Conversion of **10** *to ψ-taraxasterol.* Compound **10** (8 mg) was refluxed with Li (20 mg) and dry ethylene diamine (3 ml) in an atmosphere of N_2 for 25 min and worked-up in the usual way. TLC showed the formation of three products. The major product on separation by prep. TLC followed by repeated crystallization afforded *ψ*-taraxasterol as needles from MeOH, mp 190–193°; IR ν_{max}^{KBr} cm^{-1}: 3300, 1035; MS *m/z*: 426 [M]$^+$, 411, 408, 393, 344, 326, 218, 203, 189; ^{1}H NMR ($CDCl_3$): δ 0.78 (3 H, *s*), 0.82 (3 H, *s*), 0.86 (3 H, *s*), 0.88 3 H, *d*, *J*=7 Hz), 0.96 (3 H, *s*), 0.99 (3 H, *s*), 1.12 (3 H, *s*), 1.52 (3 H, *s*), 3.24 (*t*-like, H-1), 5.20 (1 H, *t*). (Found: C, 84.41; H, 11.56. $C_{30}H_{50}O$ requires: C, 73.93; H, 9.65%.)

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