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# LABDANE DITERPENOIDS FROM *NOLANA ROSTRATA*

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**Key Word Index**—*Nolana rostrata*; Nolanaceae; diterpenes; new labdane derivatives.

**Abstract**—Six new labdane diterpenes, methyl 3-oxo-18-hydroxylabda-8(17),13*E*-dien-15-oate, methyl 2β,3β-dihydroxylabda-8(17),13*E*-dien-15-oate, 2-oxo-labda-8(17),13*Z*-dien-15-oic acid, 3-oxo-18-acetoxylabda-8(17),13*Z*-dien-15-oic acid, 3-oxo-18-hydroxylabda-8(17),13*Z*-dien-15-oic acid, 2β,3β-dihydroxylabda-8(17),13*Z*-dien-15-oic acid, and the known compound kaempferol-3,7,4′-trimethyl ether were isolated from the aerial parts of *Nolana rostrata*. The structures of the new compounds were elucidated by spectroscopic methods.

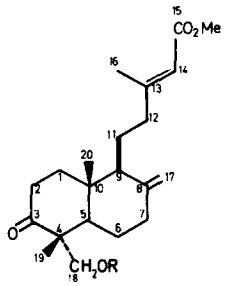
## INTRODUCTION

The genus *Nolana*, distributed in the desert and semi-desert zones of Peru and Chile, belong to the Nolanaceae family with *ca* 18 species arranged into two sections: *Alona* and *Nolana* [1]. Very little is known about the secondary metabolites of these species [1]. This paper describes the isolation and structural elucidation of six new labdane derivatives (**1a**, **1c**, **1d**, **2a**, **2b** and **3**) present in *Nolana rostrata*, a typical member of the *Alona* section, which is characterized by resinous specimens growing in Chile [1].

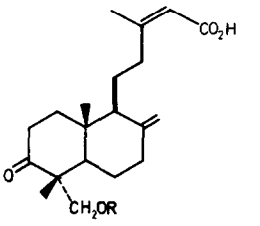
## RESULTS AND DISCUSSION

The petrol extract from the aerial parts of *N. rostrata* was subjected to column chromatography on silica gel, using increasing proportions of ethyl acetate in petrol to afford kaempferol-3,7,4′-trimethyl ether, methyl 3-oxo-18-hydroxylabda-8(17),13*E*-dien-15-oate (**1a**), methyl 2β,3β-dihydroxylabda-8(17),13*E*-dien-15-oate (**2a**), 2-oxo-labda-8(17),13*Z*-dien-15-oic acid (**3**), 3-oxo-18-acetoxylabda-8(17),13*Z*-dien-15-oic acid (**1c**), 3-oxo-18-hydroxylabda-8(17),13*Z*-dien-15-oic acid (**1d**) and 2β,3β-dihydroxylabda-8(17),13*Z*-dien-15-oic acid (**2b**).

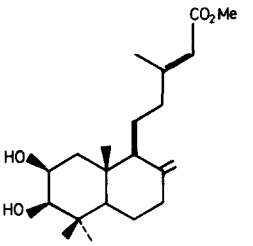
Compound **1a**, characterized as its acetate, **1b** ($C_{23}H_{34}O_5$, $[M]^+$ at *m/z* 390), showed bands for acetoxy, carbonyl and exomethylene groups in the IR spectrum and gave a typical $^1$H NMR spectrum for a labda-8(17),13*E*-diene skeleton (δ4.94, H-17; 4.62, H-17′; and 2.18, Me-16) with a primary acetoxyl group (δ4.15, *d*, *J* = 11.5 Hz, H-18; 3.98, *d*, *J* = 11.5 Hz, H-18′, AB system; and 2.05, *s*, acetyl). The spectrum also showed a three-proton singlet at δ3.70 corresponding to a carbomethoxyl group, two three-proton singlets at δ0.99 and 0.88, and a well defined doublet of double doublets at δ2.58 (*J* = 16.4, 12.2 and 6.5 Hz) was assigned to an axially orientated proton (H-2β) on an adjacent carbon to a ketone function. However, it was the $^{13}$C NMR spectrum of **1b** that provided the most information. It confirmed (Table 1) the presence of a ketone function (213.2, *s*) and an exocyclic methylene group (146.6, *s*, C-8; 108.0, *t*, C-17) [2]. The nature and *E*-geometry of the side chain of **1b**



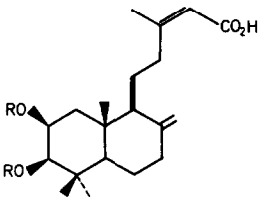

**1a** R = H
**1b** R = Ac



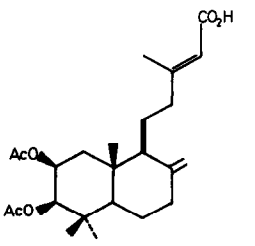

**1c** R = Ac
**1d** R = H



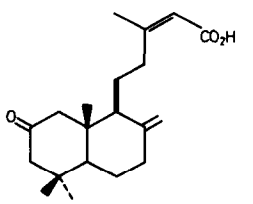

**2a**




**2b** R = H
**2c** R = Ac




**2d**




**3**

Table 1. $^{13}$C NMR spectral data of compounds **1b**, **1c**, **1d**, **2a**, **2b**, **2c**, and **3** ($CDCl_3$, TMS, SFORD)

| Carbon | 1b | 1c | 1d | 2a | 2b | 2c | 3 |
|---|---|---|---|---|---|---|---|
| 1 | 36.0 | 35.8 | 36.8 | 42.8 | 42.6 | 40.6 | 54.1 |
| 2 | 35.3 | 35.2 | 35.8 | 70.8 | 71.0 | 69.8 | 210.4 |
| 3 | 213.2 | 213.3 | 218.0 | 78.0 | 78.1 | 77.9 | 56.4 |
| 4 | 50.5 | 50.4 | 52.7 | 38.4 | 38.6 | 37.8 | 37.8 |
| 5 | 48.0 | 47.8 | 48.2 | 54.4 | 54.6 | 54.8 | 55.0 |
| 6 | 25.1 | 24.9 | 24.7 | 23.7 | 23.6 | 23.6 | 24.6 |
| 7 | 37.7 | 37.6 | 37.6 | 38.0 | 38.1 | 38.1 | 37.8 |
| 8 | 146.6 | 146.4 | 147.0 | 147.0 | 147.3 | 146.9 | 146.8 |
| 9 | 55.1 | 55.7 | 55.9 | 56.5 | 57.8 | 57.7 | 56.8 |
| 10 | 39.1 | 39.1 | 39.2 | 38.6 | 38.4 | 38.8 | 37.6 |
| 11 | 22.1 | 22.9 | 22.9 | 21.7 | 23.1 | 22.9 | 23.2 |
| 12 | 39.7 | 32.9 | 33.0 | 39.7 | 33.1 | 33.1 | 32.8 |
| 13 | 160.2 | 163.4 | 163.0 | 160.6 | 164.1 | 163.4 | 163.5 |
| 14 | 115.3 | 115.5 | 115.9 | 114.8 | 115.3 | 115.9 | 115.6 |
| 15 | 167.2 | 171.0 | 170.8 | 167.1 | 170.4 | 170.4 | 171.3 |
| 16 | 18.9 | 25.8 | 25.7 | 18.9 | 25.8 | 25.7 | 25.8 |
| 17 | 108.0 | 107.8 | 107.7 | 107.1 | 107.1 | 108.0 | 107.9 |
| 18 | 67.2 | 67.0 | 66.5 | 29.9 | 29.9 | 29.5 | 33.5 |
| 19 | 17.8 | 17.8 | 17.2 | 17.1 | 17.1 | 17.6 | 22.7 |
| 20 | 14.0 | 13.9 | 14.3 | 15.7 | 15.7 | 15.7 | 15.4 |
| COOMe | 50.8 | — | — | 50.6 | — | — | — |
| MeCO | 170.6 | 170.5 | — | — | — | 171.4, 170.6 | — |
| MeCO | 20.9 | 20.9 | — | — | — | 21.2, 20.8 | — |

was established by comparison with the $^{13}$C NMR spectral data of methyl copaiferate [3], a labdane-type diterpenoid with identical side chain to that of compound **1b**. In fact, the signals due to C-12, C-13, C-14, C-15, C-16 and the methoxyl group of methyl copaiferate appeared at very similar positions to those in the spectrum of **1b** (Table 1). The spectrum also established that the $CH_2OAc$ group was equatorially orientated (C-18) at C-4, because a *γ-gauche* effect on the C-5 was present. In addition, the location of the ketone function at C-3 was again deduced from the $^{13}$C NMR spectrum of **1b** which showed the expected deshielding effects on C-2 and C-4 and also γ-effects on the equatorial C-18 oxymethylene group and on the axial Me-19 group, in a similar fashion to that found in methyl 23-hydroxy-3-oxoolean-12-en-28-oate [4].

The assignments of the remaining signals [2, 3] are completely in accord with the proposed structure and **1b** thus corresponds to methyl 3-oxo-18-acetoxylabda-8(17),13*E*-dien-15-oate. The acetate **1b** was then hydrolysed with potassium carbonate in methanol and purified by prep. TLC, to give the pure natural product methyl 3-oxo-18-hydroxylabda-8(17),13*E*-dien-15-oate (**1a**) ($^1$H NMR: δ3.70, *d*, *J* = 11.5 Hz, H-18, and 3.36, *d*, *J* = 11.5 Hz, H-18'; AB system; IR: 3500 cm$^{-1}$).

Compound **1c** was an amorphous product with molecular formula $C_{22}H_{32}O_5$. Comparison of the $^1$H NMR spectrum of **1c** with that of **1b** showed only minor differences for the skeletal proton signals and differed in the signals due to the side chain. Clearly compound **1c** differed from **1b** in the geometry of the 13,14 double bond and the ester methyl singlet was missing. As could be deduced from the $^1$H NMR spectrum, **1c** was a labdane with a *Z*-configuration double bond (δ1.97, Me-16) [5]. The $^{13}$C NMR spectrum of **1c** (Table 1) confirmed this point. The C-12, C-13, C-14, C-15 and C-16 carbon atom resonances of **1c** were almost identical with those of the corresponding carbon atoms reported for labda-8(17)-13*Z*-dien-15-oic acid [3]. The other carbon resonances remained almost unshifted compared with those of **1b**, leading to the assignment of the structure of **1c** as 3-oxo-18-acetoxylabda-8(17),13*Z*-dien-15-oic acid.

The structure of the third compound, **1d** ($C_{20}H_{30}O_4$, $[M]^+$ at *m/z* 334) was readily deduced by comparing its spectral data with that of **1c**. In fact, the $^1$H NMR spectrum of **1d** was very similar to that of 3-oxo-18-acetoxylabda-8(17),13*Z*-dien-15-oic acid (**1c**), but the acetate methyl singlet was missing and the H-18 and H-18' signals shifted upfield from δ4.16 and 3.98 to 3.72 and 3.38, respectively. These differences between the $^1$H NMR spectra of **1d** and **1c** indicated that the new compound (**1d**) must be the deacetyl derivative of **1c**. The $^{13}$C NMR spectrum of **1d** (Table 1) confirmed all the above results and defined the proposed structure as 3-oxo-18-hydroxylabda-8(17),13*Z*-dien-15-oic acid.

The fourth diterpene, **2a**, $C_{21}H_{34}O_4$ ($[M]^+$ at *m/z* 350) showed absorptions due to hydroxyl and α,β-unsaturated ester groups. The $^1$H NMR spectrum exhibited the characteristics of a labda-8(17),13*E*-diene nucleus (δ4.90, H-17; 4.64, H-17', and 2.17, Me-16) with an ester methyl signal at δ3.70, three C-methyl singlets at δ1.02, 1.00 and 0.96, and two geminal protons to hydroxyl groups [δ4.15 (1H, *q*) and 3.23 (1H, *d*)]. The $^{13}$C NMR chemical shifts of **2a** (Table 1) closely corresponded to those of **1b** except for the A-ring carbon atoms, which showed the effects due to two β-oriented hydroxyl groups at C-2 (70.8, *d*) and C-3 (78.0, *d*), because significant shifts in the C-1, C-2, C-3, C-4, C-18 and C-19 carbon resonance signals were present as compared to a compound unsubstituted at these carbon atoms (C-2 and C-3) [2]. The assignments of the $^{13}$C NMR spectral signals of the A-ring carbon atoms of

**2a** were made on the basis of the observed multiplicities, empirical shift rules ($\alpha$, $\beta$, and $\gamma$ effects of the hydroxyl group) and comparison with the reported $^{13}$C NMR spectral data of acinosolic acid [6], a triterpenoid with an A ring identical to that of compound **2a**. Further confirmation of the $\beta$-disposition of the hydroxyl groups was obtained from the $^1$H NMR spectrum of **2a**, since the coupling constant values of its geminal protons indicated that they underwent axial–equatorial coupling. Therefore, on the basis of these data, **2a** is shown to be methyl-2$\beta$,3$\beta$-dihydroxylabda-8(17),13*E*-dien-15-oate.

Compound **2b**, $C_{20}H_{32}O_4$ ([M]$^+$ at *m/z* 336), differs from **2a** only in the absence of the ester methyl group and the presence of a *Z*-configuration for the 13,14 double bond. The $^1$H NMR spectrum showed that **2b** lacked the ester methyl singlet and the geometry of the side chain was assigned on the basis of the chemical shift of Me-16 ($\delta$1.92, *s*), which was as expected for the *Z*-isomer. The $^{13}$C NMR spectrum (Table 1) supports this structural assignment and **2b** is shown to be 2$\beta$,3$\beta$-dihydroxylabda-8(17),13*Z*-dien-15-oic acid. Acetylation of **2b** afforded two diacetate derivatives, **2c** and **2d** (see Experimental). The $^1$H NMR spectrum of **2c** showed the acetate methyl signals at $\delta$2.03 and the downfield shift of H-2 and H-3 from $\delta$4.21 and 3.23 in **2b** to 5.38 and 4.65, respectively, in the diacetate **2c**. Comparison of the A-ring $^{13}$C NMR data obtained for compound **2c** with the corresponding data published for acinosolic acid diacetate [6] allowed the location of the substituents as indicated in structure **2c**. As could be deduced from the $^1$H NMR spectra, **2c** and **2d** (see Experimental) only differed in the configuration of the side-chain double bond.

The $^1$H NMR spectrum of the last compound, **3**, $C_{20}H_{30}O_3$ ([M]$^+$ at *m/z* 318) showed the characteristics of a labda-8(17),13*Z*-diene nucleus (see Experimental) with three C-methyl singlets at $\delta$1.06, 0.84 and 0.69. However, it was the $^{13}$C NMR spectrum of **3** that provided the most information. It showed (Table 1) the presence of a ketone function (210.4, *s*), and an exo-methylene group (146.8, *s*, C-8; 107.9, *t*, C-17). The nature and *Z*-geometry of the side chain of **3** was unambiguously established by comparison of its $^{13}$C NMR spectral data with those of the corresponding carbon atoms of **1c**, **2b** and **2c**. The location of the ketone function at C-2 was also deduced from the $^{13}$C NMR spectrum, which showed the expected deshielding effects on C-1 and C-3. These assignments are in agreement with those reported for 2-keto-manoyl oxido [3]. Therefore, compound **3** corresponded to 2-oxo-labda-8(17),13*Z*-dien-15-oic acid.

## EXPERIMENTAL

Mps uncorr. $^1$H NMR: 60, 100 or 360 MHz in $CDCl_3$ with TMS. $^{13}$C NMR: 22.15 or 90.5 MHz. IR: film, $CHCl_3$ or KBr pellets. MS: direct inlet, 70 eV.

*Nolana rostrata* (Lindley) Mier, was collected in La Serena, IV-Región, Chile, in Sept. 1984. A voucher specimen is deposited at Universidad Federico Santa María.

The air dried aerial parts (1.0 kg) of *N. rostrata* were extracted at room temp. with petrol for 24 hr, affording 15.8 g of a syrup. A portion of this syrup (10 g) was chromatographed on a silica gel column (400 g) eluting with mixtures of petrol and EtOAc of increasing polarity. Fractions of 100 ml were taken and combined based upon TLC monitoring. Fraction 10 provided kaempferol-3,7,4′-trimethyl ether (110 mg). Fraction 33 gave a mixture containing **1a** (280 mg). Fractions 37–42 provided a mixture of **2a** and **3**. Fractions 77–79, after crystallization from *n*-heptane–EtOAc, gave **1c** (140 mg). Fractions 92 and 113–115 gave **1d** (200 mg) and **2b** (151 mg), respectively.

*Purification of fraction* 33. The $^1$H NMR spectrum of fraction 33 suggested the presence of one major compound with a primary OH group (**1a**). This fraction, after treatment with pyridine (0.5 ml) and $Ac_2O$ (2.0 ml) at room temp. overnight and evapn of the reagents under vacuum, was chromatographed on a silica gel column (20 g) and eluted with petrol–EtOAc (8:2), yielding **1b** (230 mg).

*Purification of* **2a** *and* **3**. Fractions 37–42 (250 mg) were rechromatographed on a silica gel column (30 g) and eluted with petrol–EtOAc (3:2) yielding pure **2a** (110 mg) and **3** (40 mg).

*Methyl 3-oxo-18-acetoxylabda-8(17),13E-dien-15-oate* (**1b**). Oil. $[\alpha]_D^{25}$ +35.4° ($CHCl_3$; *c* 0.90). IR $\nu_{max}^{film}$ cm$^{-1}$: 3080, 2960–2840, 1740, 1710, 1640, 1440, 1380, 1240, 1150, 1040, 900, 870. $^1$H NMR (360 MHz): $\delta$5.68 (1H, *q*, *J* = 1.5 Hz, H-14), 4.94 (1H, *br s*, H-17), 4.62 (1H, *br s*, H-17′), 4.15 (1H, *d*, *J* = 11.5 Hz, H-18), 3.98 (1H, *d*, *J* = 11.5 Hz, H-18′), 3.70 (3H, *s*, COOMe), 2.58 (1H, *ddd*; J = 16.4, 11.6, 6.5, H-2$\beta$), 2.46 (1H, *m*, H-7$\alpha$), 2.42 (1H, *m*, H-9$\alpha$), 2.32 (1H, *ddd*, *J* = 16.4, 9.0, 4.5, H-2$\alpha$), 2.18 (3H, *d*, *J* = 1.5 Hz, H-16), 2.08 (1H, *m*, H-7$\beta$), 2.05 (3H, *s*, $CH_2OAc$), 0.99 (3H, *s*, H-19), 0.88 (3H, *s*, H-20). $^{13}$C NMR: see Table 1. MS *m/z* (rel. int.): 390 [$C_{23}H_{34}O_5$, M]$^+$ (4), 358 [M − MeOH]$^+$ (3), 330 [M − HOAc]$^+$ (4), 316 [M − $C_3H_6O_2$]$^+$ (13), 277 [M-$C_6H_9O_2$]$^+$ (10), 255 (10), 241 (10), 201 (24), 114 (41), 107 (49), 91 (52), 82 (80), 55 (54), 43 (100), 41 (75).

*Methyl 3-oxo-18-hydroxylabda-8(17),13E-dien-15-oate* (**1a**). Compound **1b** (50 mg) was hydrolysed with $K_2CO_3$ in MeOH at room temp. under $N_2$. After 1 hr the mixture was filtered, concd and purified by prep. TLC ($R_f$ 0.55, silica gel, petrol–EtOAc, 3:2) to give **1a** (28 mg), gummy. IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3500, 3080, 3020, 2960, 2840, 1710, 1700, 1640, 1450, 1440, 1380, 1160, 900. $^1$H NMR (60 MHz): $\delta$5.65 (1H, *br s*, H-14), 4.93 (1H, *br s*, H-17), 4.58 (1H, *br s*, H-17′), 3.67 (3H, *s*, COOMe), 3.70 (1H, *d*, *J* = 11.5 Hz, H-18), 3.36 (1H, *d*, *J* = 11.5 Hz, H-18′), 2.60–2.30 (4H, *m*, H-2$\beta$, H-7$\alpha$, H-9$\alpha$ and H-2$\alpha$), 2.17 (3H, *br s*, H-16), 0.93 (3H, *s*, H-19), 0.90 (3 H, *s*, H-20). MS *m/z* (rel. int.): 348 [$C_{21}H_{32}O_4$, M]$^+$ (25), 333 [M − Me]$^+$ (17), 330 [M − $H_2O$] (38), 297 (24), 235 (15), 217 (40), 114 (38), 91 (59), 82 (100), 55 (70).

*3-Oxo-18-acetoxylabda-8(17),13Z-dien-15-oic acid* (**1c**). Amorphous powder (*n*-hexane–EtOAc); $[\alpha]_D^{25}$ +37.5° ($CHCl_3$; *c*. 1.10). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3500, 3080, 3020, 2960–2840, 1740, 1700, 1640, 1450, 1415, 1380, 1250, 1050, 900. $^1$H NMR (100 MHz): $\delta$5.68 (1H, *br s*, H-14), 4.95 (1H, *br s*, H-17), 4.77 (1H, *br s*, H-17′), 4.16 (1H, *d*, *J* = 11.4 Hz, H-18), 3.98 (1H, *d*, *J* = 11.4 Hz, H-18′) 2.60–2.30 (4H, *m*, H-2$\beta$, H-7$\alpha$, H-9$\alpha$, H-2$\alpha$), 2.07 (3H, *s*, $CH_2OAc$), 1.97 (3H, *br s*, H-16), 0.99 (3H, *s*, H-19), 0.87 (3H, *s*, H-20). $^{13}$C NMR: see Table 1. MS *m/z* (rel. int.): 376 [$C_{22}H_{32}O_5$, M]$^+$ (2), 358 [M − $H_2O$]$^+$ (2), 316 [M − HOAc]$^+$ (4), 277 [M − $C_5H_6O_2$]$^+$ (9), 217 [277 − HOAc] (7), 91 (40), 81 (40), 79 (42), 67 (49), 55 (70), 43 (100), 41 (90).

*3-Oxo-18-hydroxylabda-8(17),13Z-dien-15-oic acid* (**1d**). Mp 84–86° (*n*-heptane–EtOAc). $[\alpha]_D^{25}$ +28.5° ($CHCl_3$; *c* 2.00). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3550, 3400, 3080, 2960, 2840, 1700, 1640, 1450, 1415, 1260, 1050, 940, 900, 860. $^1$H NMR (100 MHz): $\delta$5.68 (1H, *br s*, H-14), 4.95 (1H, *br s*, H-17), 4.76 (1H, *br s*, H-17′), 3.72 (1H, *d*, *J* = 11.4 Hz, H-18), 3.38 (1H, *d*, *J* = 11.4 Hz, H-18′), 2.60–2.30 (4H, *m*, H-2$\beta$, H-7$\alpha$, H-9$\alpha$, H-2$\alpha$), 1.96 (3H, *s*, H-16), 0.95 (3H, *s*, H-19), 0.90 (3H, *s*, H-20). $^{13}$C NMR: see Table 1. MS *m/z* (rel. int.): 334 [$C_{20}H_{30}O_4$, M]$^+$ (3), 316 [M − $H_2O$]$^+$ (12), 304 (27), 287 (11), 235 [M − $C_5H_7O_2$]$^+$ (36), 206 (25), 133 (40), 116 (46), 107 (53), 95 (52), 81 (51), 79 (52), 67 (39), 55 (69), 43 (100), 41 (77).

*Methyl-2$\beta$,3$\beta$-dihydroxylabda-8(17),13E-dien-15-oate* (**2a**). Oil. $[\alpha]_D^{25}$ −52.8° ($CHCl_3$; *c* 1.08). IR $\nu_{max}^{film}$ cm$^{-1}$: 3500, 3080, 3020, 2960–2840, 1715, 1710, 1640, 1450, 1230, 1150, 1040, 900,

760. $^1$H NMR (100 MHz): $\delta$5.65 (1H, *q*, $J$ = 1 Hz, H-14), 4.90 (1H, *br s*, H-17), 4.64 (1H, *br s*, H-17'), 4.15 (1H, *q*, $J$ = 4.0 Hz, H-2$\alpha$), 3.70 (3H, *s*, COOMe), 3.23 (1H, *d*, $J$ = 4.0 Hz, H-3$\alpha$), 2.50–2.30 (2H, *m*, H-7$\alpha$ and H-9$\alpha$), 2.17 (3H, *d*, $J$ = 1.0 Hz, H-16), 1.02 (3H, *s*, H-18), 1.00 (3H, *s*, H-19), 0.96 (3H, *s*, H-20). $^{13}$C NMR: see Table 1. MS *m/z* (rel. int.): 350 [$C_{21}H_{34}O_4$, M]$^+$ (35), 335 [M – Me]$^+$ (12), 332 [M – $H_2O$]$^+$ (24), 317 [M – $H_2O$ – Me]$^+$ (21), 133 (13), 121 (21), 109 (45), 91 (27), 81 (35), 55 (36), 43 (100), 41 (60).

*2β,3β-Dihydroxylabda-*8(17),13*Z-dien-*15*-oic acid* (**2b**). Amorphous powder (*n*-heptane–EtOAc). $[\alpha]_D^{25}$ – 16.7° ($CHCl_3$; *c* 0.61). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3500, 3080, 2960, 2840, 1700, 1650, 1450, 1380, 1250, 1070, 1040, 900, 760. $^1$H NMR (100 MHz): $\delta$5.64 (1H, *br s*, H-14), 4.88 (1H, *br s*, H-17), 4.62 (1H, *br s*, H-17'), 4.21 (1H, *q*, $J$ = 4.0 Hz, H-2$\alpha$), 3.23 (1H, *d*, $J$ = 4.0 Hz, H-3$\alpha$), 2.45–2.25 (2H, *m*, H-7$\alpha$ and H-9$\alpha$), 1.92 (3H, *s*, H-16), 0.98 (3H, *s*, H-18), 0.95 (3H, *s*, H-19), 0.91 (3H, *s*,H-20). $^{13}$C NMR: see Table 1. MS *m/z* (rel. int.): 336 [$C_{20}H_{32}O_4$, M]$^+$ (3), 318 [M – $H_2O$]$^+$ (3), 303 [318 – Me]$^+$ (3), 300 [M – 2$H_2O$]$^+$ (4), 285 (6), 121 (100), 105 (80), 95 (73), 85 (66), 79 (97), 67 (54), 55 (80), 43 (76).

*2β,3β-Diacetoxylabda-*8(17),13*Z-dien-*15*-oic acid* (**2c**) *and 2β,3β-diacetoxylabda-*8(17),13E*-dien-*15*-oic acid* (**2d**). Compound **2b** (100 mg) was treated with $Ac_2O$ (3.0 ml) and pyridine (0.5 ml) at room temp. for 36 hr. After addition of EtOH, the reaction mixture was evapd to dryness under vacuum. This crude material showed two components by TLC. The substances were isolated by prep. TLC (silica gel; petrol–EtOAc, 7:3) and yield **2c** (50 mg $R_f$ 0.60) and **2d** (20 mg, $R_f$ 0.55). **2c**, white crystals, mp 122–125° (*n*-heptane–EtOAc). $[\alpha]_D^{25}$ – 55.5° ($CHCl_3$; *c* 1.0). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3450, 3080, 3020, 2960, 2840, 1740, 1700, 1650, 1450, 1380, 1250, 1040, 960, 890. $^1$H NMR (60 MHz): $\delta$5.70 (1H, *br s*, H-14), 5.38 (1H, *q*, $J$ = 4.0 Hz, H-2$\alpha$), 4.94 (1H, *br s*, H-17), 4.75 (1H, *br s*, H-17'), 4.65 (1H, *d*, $J$ = 4.0 Hz, H-3$\alpha$), 2.03 (6H, *s*, 2 × OAc), 1.93 (3H, *s*, H-16), 1.03 (3H, *s*, H-18), 0.90 (6H, *s*, H-19 and H-20). $^{13}$C NMR: see Table 1. MS *m/z* (rel. int.): 420 [$C_{24}H_{36}O_6$, M]$^+$ (15), 402 [M – $H_2O$]$^+$ (15), 360 [M – HOAc]$^+$ (40), 318 [360–$CH_2$=C=O]$^+$ (48), 300 [318 – $H_2O$]$^+$ (97), 285 (98), 261 (90), 219 (83), 201 (99), 131 (84), 43 (100). Compound **2d**, gummy. $[\alpha]_D^{25}$ – 30.3° ($CHCl_3$; *c* 0.60). IR and MS identical to those of **2c**. $^1$H NMR (60 MHz): $\delta$5.70 (1H, *br s*, H-14), 5.40 (1H, *q*, $J$ = 4.0 Hz, H-2$\alpha$), 4.97 (1H, *br s*, H-17), 4.67 (1H, *d*, $J$ = 4.0 Hz, H-3$\alpha$), 4.58 (1H, *br s*, H-17'), 2.16 (3H, *s*, H-16), 2.04 (6H, *s*, 2 × OAc), 1.02 (3H, *s*, H-18), 0.90 (6H, *s*, H-19 and H-20).

*2-Oxo-labda-*8(17),13*Z-dien-*15*-oic acid* (**3**). Gum. $[\alpha]_D^{25}$ + 55.4° ($CHCl_3$, *c* 0.81). IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 3080, 2960–2840, 1700, 1650, 1450, 1415, 1380, 1250, 900. $^1$H NMR (100 MHz): $\delta$5.68 (1H, *br s*, H-14), 4.94 (1H, *br s*, H-17), 4.73 (1H, *br s*, H-17'), 2.60–2.50 (2H, *m*, H-1$\alpha$ and H-3$\alpha$), 1.93 (3H, *br s*, H-16), 1.06 (3H, *s*, H-18), 0.84 (3H, *s*, H-20), 0.69 (3H, *s*, H-19). $^{13}$C NMR: see Table 1. MS *m/z* (rel. int.): 318 [$C_{20}H_{30}O_3$, M]$^+$ (34), 303 [M – Me]$^+$ (25), 300 [M – $H_2O$]$^+$ (32), 285 [M – Me – $H_2O$]$^+$ (22), 219 [M – $C_5H_7O_2$]$^+$ (57), 151 (65), 135 (30), 91 (68), 82 (90), 69 (70), 55 (82), 43 (62), 41 (100).

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