178. New Carbonyl Compounds in the High-Boiling Fraction of Lavender Oil

1st Communication[1])

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Summary

A series of new carbonyl compounds with santalane (**3–9**) as well as cadinane skeleton (**10–13**) have been identified for the first time in lavender oil. Most of the structures established by spectra interpretation are corroborated by partial synthesis starting from well-defined natural products.

Introduction. – The oils of lavender (*Lavandula officinalis* CHAIX) and lavandin (Hybrid of *Lavandula officinalis* CHAIX and *L. latifolia* VILL.) are certainly among the most popular and important essential oils. The high interest in these oils is very well reflected by the plurality of investigations concerning their compositions, e.g. [1–16].

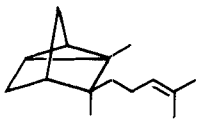
Although about 300 constituents could be identified in the course of our first analytical study a series of minor and trace constituents localized by GLC/MS measurements of representative fractions could not be elucidated at that time. We therefore reinvestigated this interesting oil taking advantage of the considerable progress achieved since then in instrumental methods. In the following series of communications we discuss some new carbonyl components identified in the high-boiling fraction of lavander oil.

Isolation of the High-Boiling Carbonyl Fraction. – French lavender oil (9.0 kg, 40–42%), concentrated by removal of 98% of the volatiles (b.p. up to 120°/12 Torr), served as starting material. The remaining high-boilers were once again distilled using a *Widmer* column (15 cm) to give a fraction of 126.5 g (92–145°/0.06 Torr) which was treated with *Girard* reagent *P*. The decomposition of the *Girard* condensation products in aqueous, slightly acidic medium yielded a high-boiling carbonyl fraction of 9.80 g (0.11% by weight of the total oil). This fraction was separated by silica-gel column chromatography according to the polarity of the individual constituents using a hexane/ether gradient from 40 : 1 to 1 : 5. The fractions obtained were checked by GLC, and afterwards the representative ones were thoroughly inves-

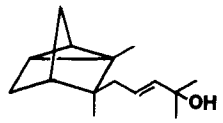
[1]) Partially presented at the '13th International Workshop on Essential Oils', Würzburg (Germany), September 7–11, 1982.

tigated by means of GLC/MS measurements. The unknown compounds were further enriched as far as possible and finally isolated by preparative GLC to determine their structures.

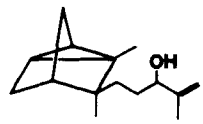
A. *Sesquiterpene Derivatives with Santalane Skeleton.* As already reported [16], lavender oil contains in opposition to sandalwood oil (−)-α-santalene, from which the lavender constituents (+)-α-photosantalol A, α-photosantalol B, (−)-α-nor-santalenone (**1**) and α-santalal (**2**) are derived[2]).



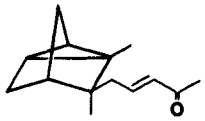
(−)-α-Santalene



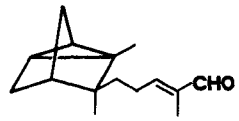
(+)-α-Photosantalol A



α-Photosantalol B



1 (0.3%)



2 (0.2%)

The separation of the high-boiling carbonyl fraction by column chromatography (hexane/ether 40:1) led to fractions containing two new components with santalane skeleton. On the basis of the spectral data of the purified products the presence of the α-santalan-12-one (**3**) and the α-santal-13-en-12-one (**4**) is presumed[2]).

From more polar fractions (hexane/ether 10:1) we could also isolate the new 13-hydroxy-α-santalan-12-one (**5**)[2]) which gave **4** on dehydration with $KHSO_4$ in toluene.

Compounds **3** and **4** exhibit a fruity-woody odor whereas **5** is nearly odorless.

The structures **3**–**5** were confirmed by synthesis starting from (+)-α-santalene *ex* sandalwood oil *via* the already mentioned α-photosantalol B *(Scheme 1)*. Oxidation of α-photosantalol B with MnO_2 in pentane gave (+)-**4** showing the same spectral data as the isolated product. Hydrogenation of (+)-**4** using PtO_2 as catalyst and ethanol as solvent furnished (+)-**3**.

As degradation products of the discussed santalene derivatives we identified in the more volatile part of the carbonyl fraction teresantalal (**6**), nortricyclo-eka-santalal (**7**), tricyclo-eka-santalal (**8**) and dehydrotricyclo-eka-santalal (**9**)[2]).

Compounds **6**–**8** have been already reported as constituents of East Indian sandalwood oil [17] whereas no other natural occurrence for **9**[3]) is known up to now.

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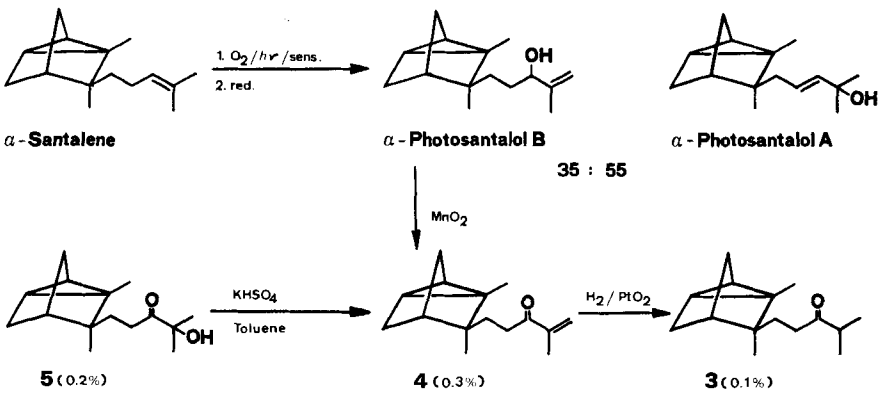
[2]) The percentages in parentheses given beneath the corresponding formula are approximate values based on the total carbonyl fraction of lavender oil.

[3]) Compound **9** as well as **12** were independently identified in the same substrate by *Ch. Ehret, Roure-Bertrand-Dupont* (private communication).

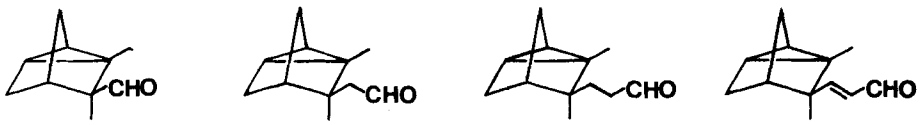
Scheme 1



		$[\alpha]_D$	c/100 ml $CHCl_3$
α-santalan-12-one (**3**)	*ex* lavender	−15.8°	0.38
α-santalan-12-one (**3**)	*ex* (+)-α-santalene	+17.8°	2.06
α-santal-13-en-12-one (**4**)	*ex* lavender	−10.2°	0.55
α-santal-13-en-12-one (**4**)	*ex* (+)-α-santalene	+11.2°	1.11

The structure of **9** was established by interpretation of the spectral data and by hydrogenation to the known aldehyde **8**. Degradation products **6** and **7** have a sweetish-camphoraceous odor whereas **8** and **9** possess already typical sandalwood aspects.

For spectral comparison **8** was prepared by ozonolysis of α-santalol [18]. As described in [19] the ozonolysis of the enol acetate of **8** finally furnished the trisnoraldehyde **7**.



6 (trace) **7 (0.1%)** **8 (0.8%)** **9 (0.4%)**

Since all these aldehydes are very sensitive to autoxidation we were not surprised to identify the acids corresponding to **6**–**9** in the acidic part of lavender oil.

B. *Sesquiterpene Derivatives with Cadinane Skeleton. – Two Isomers of 14-Norcadin-5-en-4-one.* One of the dominating main constituents of the high-boiling carbonyl fraction (*ca.* 1%) was eluted with hexane/ether 10:1. The spectral data of the purified product were identical with those of the synthetically prepared 14-norcadin-5-en-4-one (**10**) [20].

With the aid of GLC/MS measurements, the isomer **11** with the equatorial isopropyl group at C(7) could also be identified as a minor constituent (0.1%).

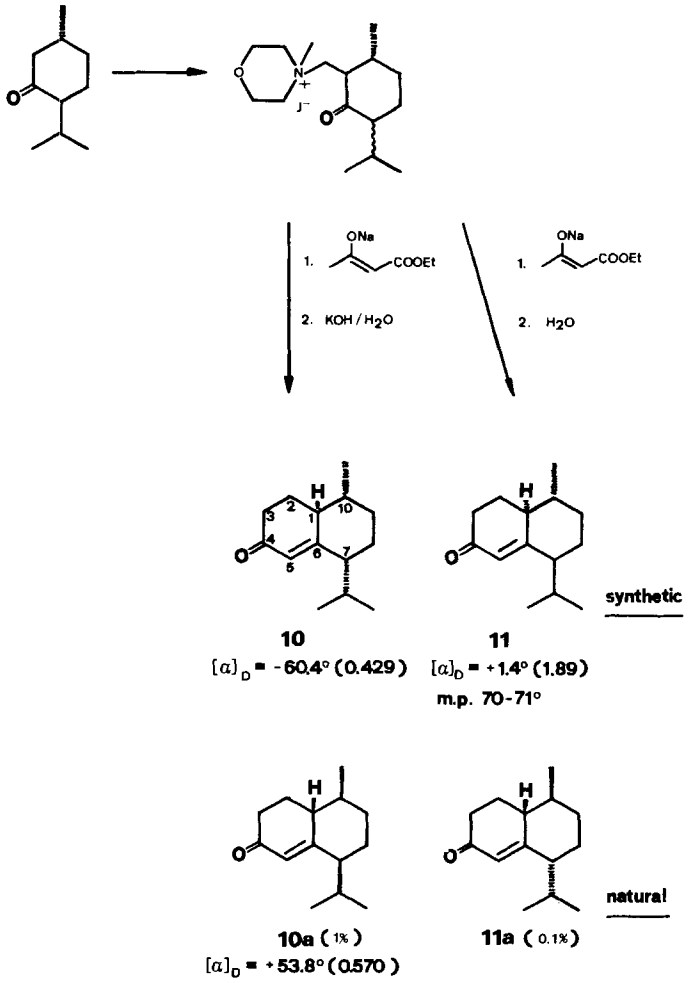
Since the norcadinenone **10**, synthetically obtained from (−)-menthone, shows the opposite optical rotation to the sample isolated from lavender oil, the absolute configuration of the naturally occurring product should be established as **10a** and, consequently, of the natural sample of **11** as **11a**.

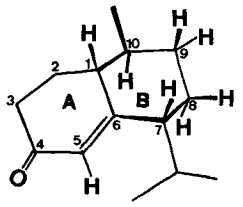
As depicted in *Scheme 2*, **11** seems to be kinetically controlled. In fact, treatment of pure **11** with KOH in ethanol leads to the thermodynamically more stable isomer **10** with the axial isopropyl group.

Already in 1973 *Mookherjee & Trenkle* [15] isolated **10** from lavandin oil as so-called peak *23-A* and published the corresponding IR and mass spectra. Due to the lack of material NMR analysis of this peak could not be performed, and therefore a structural assignment was not possible at that time.

Independent of mechanistic considerations and informations obtained from the CD spectra, the configuration of **11** – and consequently also of **10** – can be established by interpretation of their 400-MHz ^{1}H-NMR spectra. Regarding **11**, it is possible to localize two secondary axial protons in ring B both of them having two

Scheme 2





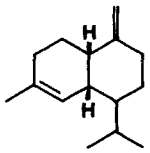
11

axial neighboring protons. Consequently, H–C(7) and H–C(10) have to be axial, and therefore the *trans*-configuration of isopropyl-C(7) to CH_3–C(10) is clearly established. Furthermore H–C(10) appears after decoupling of CH_3–C(10) as a *td* with $J(H(1)_{ax}–H(10)_{ax}) = J(H(9)_{ax}–H(10)_{ax}) = 11$ Hz and $J(H(9)_{eq}–H(10)_{ax}) =$ 3.5 Hz indicating the axial positions of H–C(1) as well as H–C(10). An additional support for this *trans*-configuration is given by the splitting pattern for H–C(5). The *t*-like shape of the signal corresponding to H–C(5) in **11** at 5.86 ppm is compatible with the presence of two pseudo-axial allylic protons in positions 1 and 7, respectively. In the case of **10**, however, only one allylic coupling with H–C(1) results in a *d*-structure ($J \approx 2$ Hz) for H–C(5) at 5.82 ppm.

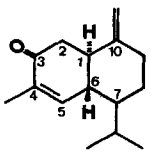
Based on the interpretation of the half-width value for H–C(5) in **10** and **11**, *Belavadi & Kulkarni* [21] obtained the reverse assignment but revised it very recently [22]. Their correction is based on the work of *Wilson & Misra* [23]. In connection with the total synthesis of epizonarene these authors unequivocally established the configuration of the crystalline minor isomer **11** of a racemic synthetic mixture by X-ray diffraction.

Cadina-4,10(15)-dien-3-one. Another new lavender constituent present to 0.5% in the total carbonyl fraction was eluted with hexane/ether 40:1 and showed after its purification an optical rotation of + 112.7° (c = 0.316, $CHCl_3$). The ^{1}H-NMR data of this dienone are compatible with those of the cadina-4,10(15)-dien-3-one (**12**) synthesized by *Kelly & Eber* [24] in connection with the structural elucidation of khusinol.

In the ^{1}H-NMR spectrum of **12** the signal for H–C(7) at 1.39 ppm shows two large coupling constants of 12 Hz each indicating the axial position of H–C(7) as well as the axial position of two neighboring protons, namely H–C(6) and one of H–C(8). In the spectrum with well-separated signals after addition of a sufficient amount of Eu(fod)$_3$, the axial H–C(6) and H–C(1) appear as *t* with coupling

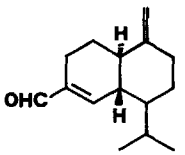


γ-Cadinene



12 (0.05%)

$(\alpha)_D$ = + 112.7° (0.316)



13 (0.1%)

constants of 11 Hz each. Consequently, H–C(1) has also to be axial meaning a *trans*-fused ring system. As already discussed [22] this *trans*-fused structure is in agreement with the *s* for the olefinic proton at 6.88 ppm since the model shows a dihedral angle of *ca.* 90° between H–C(5) and H–C(6).

Based on comparison of the ^{1}H-NMR data with those of **12**, the structure **13** can be proposed for a slightly less polar aldehyde of the same molecular weight. Compounds **12** and **13** can be considered as oxidation products of γ-cadiene also present on lavender oil.

We wish to express our gratitude to Dr. *E. Billeter* and Mrs. *G. Scribano* from our physical chemistry department for many in-depth NMR studies and valuable discussions. We are also thankful to Mrs. *M. Hug-Inderbitzin* for the synthesis of the norcadinenones **10** and **11**.

Experimental Part

(With the valuable collaboration of Mr. *E. Schwendener* and Mr. *E. Stocker*)

General. Specific rotations $[\alpha]_D^{20}$ were measured in a 10-cm tube using $CHCl_3$ as solvent on a *Perkin-Elmer* Model *141* polarimeter (concentration *c* in parentheses). Melting points (m.p.) are uncorrected. Prep. column chromatography (CC) was performed on silica gel *Merck* (particle size 0.05–0.2 mm). Gas chromatography (GC) was run on *Carlo Erba* Models *FTV G 1* and *FTV 4160* (*Carbowax 20M*, 3 m × 3 mm, packed columns; *UCON HB 5100* and *Pluronic L 64*, 50 m × 0.3 mm, glass capillary columns). For prep. separations a *Carlo Erba* Model *GV* was used (*Carbowax 20M*, 3 m × 15 mm). Spectra were recorded on the following apparatus: UV: *Beckman DB-G* spectrophotometer (λ_{max} in nm, ε in parentheses); IR: *Perkin-Elmer 257*; characteristic band positions are given in cm^{-1}; ^{1}H-NMR: *Varian-EM 360*, *Bruker WH-360* and *WH-400*. Measurements were run in $CDCl_3$ with TMS (0 ppm) as internal standard. Abbreviations: *s* = singlet; *d* = doublet; *t* = triplet; *q* = quartet; *m* = multiplet; br. = broad; ax = axial; eq = equatorial; *J* = apparent coupling constant in Hz; MS: *Variant MAT*, Models *CH-5* and *212* (70 eV), the molecular ions (M^+) and fragment ions are given as *m/z* with relative peak intensities in % of the base peak. The same apparatus were used for GC/MS measurements.

Partial Synthesis of the Santalene Derivatives **3** *and* **4**. – *α-Santal-13-en-12-one* (**4**). To a solution of 1.35 g (6.14 mmol) α-photosantalol B (obtained *via* sensitized photo-oxygenation of (+)-α-santalene *ex* sandalwood oil [16]) in 60 ml pentane were added 15.0 g MnO_2 (*Merck*, activated 14 h at 120°) and the suspension stirred for 14 h. After filtration, the solution was concentrated and the residue distilled to obtain 0.90 g (67%) of **4**, b.p. 68–70°/0.02 Torr (Kugelrohr), purity > 98% (GC). IR (neat): 1678, 1632, 1092, 1075, 1039, 928, 850. ^{1}H-NMR (400 MHz): 0.83 (*s*, 3 H); 0.86 (br. *s*, 2 H); 1.02 (*s*, 3 H); 1.05 (*m*, 2 H); 1.40–1.65 (*m*, 5 H); 1.87 (*s*, 3 H); 2.60 (*m*, 2 H); 5.76 (*s*, 1 H); 5.95 (*s*, 1 H). MS: 218 (10, M^+), 175 (19), 160 (17), 147 (16), 134 (16), 121 (43), 119 (49), 105 (29), 93 (100), 91 (41), 84 (12), 77 (21), 69 (43), 41 (68).

α-Santalan-12-one (**3**). The ketone **4** (0.50 g) in 5 ml EtOH was hydrogenated in the presence of 0.020 g of 10% Pd/C. After 15 min, the theoretical amount of H_2 had been absorbed. The catalyst was removed by filtration and the residue distilled to obtain 0.35 g (70%) of **3** (purity > 95%), b.p. 68–72°/0.02 Torr (Kugelrohr). IR (neat): 1712, 1085, 1068, 1035, 1010, 983, 850. ^{1}H-NMR (400 MHz): 0.80 (*s*, 3 H); 0.86 (br. *s*, 2 H); 1.02 (*s*, 3 H); 1.05 (*m*, 2 H); 1.10 (*d*, $J \approx 7$, 6 H); 1.40–1.65 (*m*, 5 H); 2.37 (*m*, 2 H); 2.63 (*m*, $J \approx 7$, 1 H). MS: 220 (36, M^+), 177 (27), 134 (28), 121 (66), 119 (39), 111 (16), 105 (24), 93 (100), 91 (38), 79 (28), 71 (59), 43 (95), 41 (43).

13-Hydroxy-α-santalan-12-one (**5**). $[\alpha]_D^{20} = -5.7°$ ($c = 0.935$). IR: 3470, 1708, 1168, 1067, 970, 850. ^{1}H-NMR (400 MHz): 0.82 (*s*, 3 H); 0.86 (*m*, 2 H); 1.03 (*s*, 3 H); 1.08 (*m*, 2 H); 1.39 (*s*, 6 H); 1.40–1.65 (*m*, 5 H); 2.46 (*m*, 2 H). MS: 236 (< 1, M^+), 178 (4), 160 (1), 145 (2), 135 (3), 121 (8), 111 (10), 93 (15), 79 (6), 67 (4), 59 (100), 41 (10).

Dehydration of **5** *to* **4**. The ketone **5** (15 mg) in 5 ml toluene and 5 mg $KHSO_4$ were stirred for 15 min at 100°. The product after usual workup showed after its purification by GC same spectral features as **4** (see above).

Degradation Products of Santalene Derivatives. For spectral data of **6**–**8** see [17].

Dehydrotricyclo-eka-santalal (**9**). IR ($CHCl_3$): 3040, 2700, 1678, 1620, 980. ^{1}H-NMR (400 MHz): 1.03 and 1.08 (2 *s*, 6 H); 0.97–1.27 (*m*, 4 H); 1.60–1.82 (*m*, 3 H); 6.15 (*dd*, J = 16, J = 8, 1 H); 6.86 (*d*, J = 16, 1 H); 9.50 (*d*, J = 8, 1 H). MS: 176 (13, M^+), 147 (61), 119 (33), 108 (40), 105 (67), 95 (54), 93 (66), 91 (83), 83 (35), 79 (100), 65 (28), 55 (87), 41 (79).

Compound **9** (10 mg) in 1 ml hexane was hydrogenated in the presence of a small amount of 10% Pd/C. After 5 min the catalyst was removed by filtration and the product purified by GC. The product (5 mg) showed the same spectral data as **8**.

14-Norcadin-5-en-4-ones **10** *and* **11**. Following the procedure described in [20] **10** and **11** were obtained in a ratio of *ca.* 4:1. Pure **10** could be isolated from this mixture by CC on silica gel using hexane/Et_2O 10:1 as eluent. If only H_2O was added after the reaction of 2-morpholinomethyl menthone methiodide with the Na-salt of ethyl acetoacetate **10** and **11** were obtained in a reversed ratio of *ca.* 1:4. Compound **11** was isolated in a purity >99% by recrystallization of the 1:4-mixture from EtOH (m.p. 70–71°).

Equilibration of **11**. A solution of 0.60 g **11** in 5 ml EtOH and 2 ml NaOH (40%) was heated under reflux for 3 h. Usual workup led to 0.55 g of 4:1-mixture of **10** and **11**.

10. UV (EtOH): 241 (15,600). IR (neat): 1678, 1618, 1255, 1242, 1206, 1181, 1160, 1090, 1058, 983, 952, 868. ^{1}H-NMR (400 MHz): 0.77 and 0.97 (2 *d*, J = 6, 2 CH_3–C(12)); 1.03 (*d*, J = 6, CH_3–C(10)); 1.35–1.46 (*m*, 2 H); 1.48–1.60 (*m*, 2 H); 1.63–1.75 (*m*, 1 H); 1.82–1.92 (*m*, 2 H); 1.95–2.03 (*m*, 2 H); 2.18–2.29 (*m*, 1 H); 2.35–2.43 (*m*, 1 H); 5.82 (*d*, $J \approx 2$, H–C(5)). MS: 206 (40, M^+), 164 (100), 163 (28), 149 (31), 136 (15), 122 (28), 121 (27), 107 (18), 91 (19), 79 (17), 55 (13), 41 (17).

11. UV (EtOH): 240 (15,200). IR ($CHCl_3$): 1665, 1615, 988, 963, 925, 878. ^{1}H-NMR (400 MHz): 0.89 and 0.97 (2 *d*, J = 7, 2 CH_3–C(12)); 1.03 (*d*, J = 7, CH_3–C(10)); 1.15 (*qd*, $J(8_{ax},9_{eq}) = 3.5$, $J_{gem}(8_{ax},8_{eq}) = J(8_{ax},9_{ax}) = J(8_{ax},7_{ax}) = 12.5$, H_{ax}–C(8)); 1.25 (*qd*, $J(9_{ax},8_{eq}) = 3.5$, $J_{gem}(9_{ax},9_{eq}) = J(9_{ax},8_{ax}) = J(9_{ax},10_{ax}) = 12.5$, H_{ax}–C(9)); 1.52 (*m*, H_{ax}–C(10)); 1.80 (*m*, H_{eq}–C(2)); 1.80–1.92 (*m*, H_{ax}–C(1), H_{ax}–C(7), H_{eq}–C(9)); 2.00 (*m*, H_{eq}–C(8)); 2.02 (*m*, H–C(12)); 2.17 (*m*, 3x J = 10, J = 5, H_{ax}–C(2)); 2.27 and 2.38 (*ddd*, *ABXY*-system, J = 16, J = 9, J = 5, 2 H–C(3)); 5.86 (*t*-like *s*, H–C(5)). MS: 206 (41, M^+), 164 (100), 163 (28), 149 (26), 136 (17), 121 (36), 107 (25), 91 (31), 79 (29), 55 (21), 41 (35).

Cadina-4,10(15)-dien-3-one (**12**). M.p. 69–70°. UV (EtOH): 238 (9,600). IR ($CHCl_3$): 1670, 1139, 1112, 1086, 890. ^{1}H-NMR (400 MHz): 0.80 and 1.00 (2 *d*, J = 7, 2 CH_3–C(12)); 1.21 (*qd*, $J(8_{ax},9_{eq}) = 4$, $J_{gem}(8_{ax},8_{eq}) = J(8_{ax},9_{ax}) = J(8_{ax},7_{ax}) = 12.5$, H_{ax}–C(8)); 1.39 (*tt*, $J(7_{ax},8_{eq}) = 3.5$, $J(7_{ax},8_{ax}) = J(7_{ax},6_{ax}) = 12$, H_{ax}–C(7)); 1.81 (*q*, $J \approx 2$, $J \approx 1.5$, CH_3–C(4)); 1.85 (*qd*, $J(8_{eq},7_{ax}) = J(8_{eq},9_{eq}) = J(8_{eq},9_{ax}) = 3.5$, $J_{gem}(8_{eq},8_{ax}) = 12.5$, H_{eq}–C(8)); 2.00 (*t* with fine structure, $J(6_{ax},7_{ax}) = J(6_{ax},1_{ax}) = 12$, H_{ax}–C(6)); 2.05 (*td*, $J(9_{ax},8_{eq}) = 3.5$, $J_{gem}(9_{ax},9_{eq}) = J(9_{ax},8_{ax}) = 12.5$, H_{ax}–C(9)); 2.27 (*sept.* × *d*, $J(12,13,14) = 7$, $J(12,7_{ax}) = 3$, H–C(12)); 2.38 (*m*, 2 H–C(2)); 2.42 (*dt*, $J(9_{eq},8_{eq}) = J(9_{eq},8_{ax}) = 3.5$, $J_{gem}(9_{eq},9_{ax}) = 12$, H_{eq}–C(9)); 2.68 (*dt*, $J(1_{ax},2_{pseudoax}) = J(1_{ax},2_{pseudoeq}) = 10$, $J(1_{ax},6_{ax}) = 12$, H_{ax}–C(1)); 4.54 and 4.76 (2 *s*, 2 H–C(11)); 6.88 (*s*, H–C(5)). MS: 218 (25, M^+), 190 (22), 175 (35), 147 (100), 133 (24), 119 (27), 105 (42), 91 (43), 79 (29), 69 (57), 55 (28), 41 (70).

γ-Cadinen-15-al (**13**). IR ($CHCl_3$): 1680, 1650, 1640, 1181, 1125, 1067, 908. ^{1}H-NMR (400 MHz): 0.82 and 1.00 (2 *d*, J = 7, 2 CH_3–C(12)); 1.21 (*qd*, J = 4, 3 × J = 12.5, 1 H); 1.42 (*tt*, J = 3.5, J = 12 and 12, 1 H); 1.45 (*m*, 1 H); 1.84–1.98 (*m*, 3 H); 2.02–2.17 (*m*, 3 H); 2.27 (*sept.* × *d*, J = 7, J = 3, H–C(12)); 2.40–2.55 (*m*, 2 H); 4.63 and 4.74 (2 *s*, 2 H–C(11)); 6.92 (*s*, H–C(5)); 9.47 (*s*, 1 H). MS: 218 (32, M^+), 175 (40), 157 (45), 148 (45), 147 (45), 133 (57), 105 (65), 91 (90), 79 (67), 67 (39), 55 (36), 41 (100).

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