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The Sesquiterpenoid Contents of Fruit Bodies of *Russula delica*

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The sesquiterpenoids extracted from both intact injured fruit bodies of *Russula delica* (Russulaceae) with EtOAc and dichloromethane have been investigated. The dichloromethane extract of intact specimens contained stearoyldelicone (**2b**) (75%) and stearoylplorantinone B (**3b**) (25%), while the EtOAc extracts contained comparable amounts of **3b**, no **2b** but instead the illudalane **9e**. The latter is believed to be an artifact due to the reaction between **2b** and acetic acid, produced by hydrolysis of the solvent by esterases present in the fruit bodies. EtOAc has, with good results, routinely been employed as an extraction solvent for fruit bodies of species belonging to Russulaceae, but is obviously degradable by some species and should be used with caution. In injured fruit bodies of *R. delica*, the stearic acid esters are converted into a series of free sesquiterpenes, and the isolation of four new compounds [plorantinone D (**4b**), epiplorantinone B (**5a**), deliquinone (**7**) and 2,9-epoxydeliquinone (**8**)], obtained from both EtOAc and dichloromethane extracts of injured specimens, is described.

The fruit bodies of species belonging to the Russulaceae family (genera *Russula* and *Lactarius*) have been shown to contain sesquiterpenes of several different skeletons.[1,2] In general, the intact fruit bodies contain a fatty acid ester of a precursor sesquiterpene, which, as a response to injury, is hydrolysed enzymatically and converted into different products possessing various bioactivities. The products are responsible for the characteristic pungent taste and some of the colours of the Russulaceae fruit bodies, and it has been suggested that the conversions of sesquiterpenes constitute chemical defence systems that protect the fruit bodies against parasites.[3] The most widespread precursor in these conversions is the marasmane sesquiterpenoid stearoylvelutinal (**1b**). It has been found in a number of pungent species,[1,2,4] for example *Lactarius vellereus*, *L. piperatus*, *L. rufus*, *Russula queletii*, and *R. cuprea*, in which it is converted into pungent and antibiotic unsaturated dialdehydes as a response to injury. However, the velutinal esters (e.g., **1b**) may also be chemically transformed during the extraction of the fruit bodies and the work-up of the extracts. If they come in contact with, for instance, reagent-grade solvents or silica gel, they are rapidly transformed into furanoid lactarane and *seco*-lactarane sesquiterpenes.[5] In order to obtain the true natural products it is therefore important to use mild extraction and work-up conditions, and this also applies to the species investigated here. A dichloromethane extract of intact fruit bodies of *Russula delica* contains mainly stearoyldelicone (**2b**),[6] which, in analogy with stearoylvelutinal, is sensitive to traces of acid and is efficiently transformed into the illudalane alcohol (**9b**) during chromatography on silica gel.[6] However, when the intact fruit bodies were extracted with EtOAc, the extract contained no trace of stearoyldelicone (**2b**). As EtOAc, if properly purified prior to use, is considered to be a suitable solvent and has frequently been used for the extraction of fruit bodies, we felt it necessary to investigate and understand this discrepancy between the two types of extract of intact specimens of *R. delica*. In addition, a detailed analysis of the sesquiterpenes formed from the sesquiterpenoid precursors by the enzymatic conversions initiated by injury to the fruit bodies of *R. delica* was carried out.

Results and discussion

Differences between extracts prepared with dichloromethane and ethyl acetate. A dichloromethane extract of intact fruit bodies of *R. delica* was found to contain two sesquiterpenoids, stearoyldelicone (**2b**) and stearoylplorantinone B (**3b**). From the integrals in the ^{1}H NMR spectra of the crude extract, the relative amounts were found to be approximately 3 : 1. Although **2b** and **3b** are closely related, we did not observe any interconversion

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between the two during extraction, fractionation or storage. The conclusion is therefore that both are originally present in the intact fruit bodies of *R. delica*, in contrast with the normal situation in Russulaceae species in which there is only one sesquiterpenoid as precursor. An EtOAc extract of intact fruit bodies of *R. delica* contains comparable amounts of stearoylplorantinone B (**3b**), but no stearoyldelicone (**2b**) at all. The major component is instead the acetate **9e**, which is not present in the dichloromethane extract, and it is reasonable to assume that it is formed from stearoyldelicone (**2b**). In view of the sensitivity of **2b** towards acidic conditions, one could imagine that if the EtOAc used for the extraction contained acetic acid, this could account for the transformation of **2b** into **9e** during the concentration of the extract. However, only purified EtOAc, free from acetic acid, was used for the extraction. Instead we believe that the esterases present in the fruit bodies, and which cause hydrolysis of the fatty acid esters as a response to injury (e.g., **3b** to **3a**, *vide infra*), may also hydrolyse significant amounts of the solvent to acetic acid and ethanol.

Except for one compound, no significant differences between the EtOAc and dichloromethane extracts of injured fruit bodies were observed. The exception is acetylplorantinone B (**3c**) which was obtained only from the EtOAc and not from the dichloromethane extract. Again, it is reasonable that the acetyl group originates from the solvent, possibly via regeneration of the esterases responsible for hydrolysing ethyl acetate.

A model extract of stearoyldelicone (**2b**) in ethyl acetate containing traces of acetic acid was prepared, and when evaporated on a rotary evaporator at 35 °C (see Experimental for details) **2b** was transformed quantitatively into **9e**. Plorantinone B (**3a**) and stearoylplorantinone B (**3b**) may also be transformed into the corresponding illudalanes by acetic acid, although at a considerably slower rate. Furthermore, mixtures of C-4 fatty acid esters of the illudalane alcohol **9b** were obtained in small amounts from both kinds of extract of intact fruit bodies, indicating that free fatty acids (stearic, oleic and palmitic acid) present in the extracts may also react with **2b** during the extraction procedure. The ^{1}H NMR spectra of such mixtures showed that C-4 was acylated, while mass spectra indicated the presence of **9b** acylated by stearic acid (*m/z* 782), oleic acid (*m/z* 780), and palmitic acid (*m/z* 754). Attempts to produce free delicone (**2a**) by transesterification of **2b** with catalytic amounts of potassium methoxide in MeOH at room temperature, as previously reported for stearoylvelutinal (**1a**),[7] were not successful, and the only product that could be isolated from such reactions was the adduct **6**. This indicates that delicone derivatives are electrophilic, and thus potentially toxic, and that C-6 and not C-2 is the preferred site for nucleophilic attack.

New compounds isolated in this investigation. The isolation of plorantinones A (**4a**), B (**3a**) and C (**4c**) from the EtOAc extracts of injured fruit bodies has already been reported.[8] During this reinvestigation we could, in addition, obtain plorantinone D (**4b**) from the extracts of injured specimens, although only in small amounts. The plorantinones can be viewed as products obtained by hydrolysis of the stearic ester **3b** to **3a**, followed by oxidation and/or reduction, although the precursor may also be stearoyldelicone (**2b**). In addition, the C-11 epimer of plorantinone B, *epi*-plorantinone B (**5a**), could be isolated from both extracts. Its spectral data are very similar to those of **3a**, but significant correlations (e.g. between 12-H_3 and 15-H_2) in the NOESY spectrum clearly demonstrated the difference between the two. The amounts of **5a** are smaller compared with its epimer **3a**, only approximately 15%, but there was no sign of the corresponding precursor **5b**. The two epimers **3a** and **5a** are surprisingly easily separated by straight-phase chromatography and it is reasonable to believe that this would also be the case for the two stearic acid esters **3b** and **5b**. However, even if they formed an inseparable mixture, one would expect to see the ^{1}H NMR signals for **5b** in the proton spectrum of **3b**. An example is the signal for 10-Hβ, which appears as a double doublet at 2.22 ppm in the spectrum of **3a** and at 2.34 ppm in the spectrum of **3b** (the shift difference being caused by the stearoyl group in **3b**). In the spectrum of **5a**, this signal is significantly shifted because the hydroxymethyl group is on the other side of the five-membered ring, and appears as a dd at 1.98 ppm. If our sample of **3b** contained small amounts of **5b**, a signal for 10-Hβ of **5b** would be expected to appear close to 1.98 ppm and certainly be found between 1.70 and 2.30 ppm. The only signal that could be seen in this region in the spectrum of **3b** was a doublet due to 1-Hα (at 2.04 ppm), and there was no trace of a double doublet. The formation of both epimers **3a** or **3b** as a result of the enzymatic conversions initiated by injury is puzzling. It is difficult to imagine an enzymatic epimerisation, and a C-14 reduction/C-15 oxidation is also unlikely, and this remains to be investigated.

Two new 12-norsesquiterpenes were also obtained in small amounts from both extracts of injured fruit bodies, deliquinone (**7**) and 2,9-epoxydeliquinone (**8**). Deliquinone **7** is a C-14 reduced derivative of puraquinonic acid, an inducer of differentiation of mammalian cells reported from the fungus *Mycena pura*.[9] It is, at this moment, not clear how compounds **7** and **8** are formed, because their formation requires oxidation of C-12 in the original esters (**2b** or **3b**) and no such intermediates have been identified.

The origin of the illudane **10**, present in small amounts in both extracts of injured specimens, is also unclear, as it is the only sesquiterpenoid obtained from *R. delica* lacking a hydroxy group at C-14 or C-15. Illudane **10** has previously been reported from submerged cultures of the Basidiomycete *Agrocybe aegerita*,[10] but with no indication of the stereochemistry. However, NOESY correlations observed in this investigation between 1-Hα and 12-H_3, and between 1-Hβ and 2-H, clearly showed

Table 1. ^{1}H NMR data (δ; mult.; *J*) for plorantinone D (**4b**), epiplorantinone B (**5a**), deliquinone (**7**) and 2,9-epoxydeliquinone (**8**) in $CDCl_3$.

H	4b	5a	7	8
1α	1.52; dd; 14.5, 5.4	2.28; d; 14.6	2.51; m	1.94; d; 14.8
1β	1.70; dd; 14.5, 9.7	1.35; d; 14.6	2.82; m	2.41; dd; 14.8, 1.9
2	2.66; ddd; 5.4, 9.7, 10.4	—	—	—
4α	1.91; dd; 1.9, 12.3	1.68; m; 3.4	3.75; t; 6.5	3.75; m
4β	2.20; dd; 6.4, 12.3	2.61; m; 8.6	3.75; t; 6.5	3.68; m
5α	—	2.99; m; 8.6, 16.5	2.78; t; 6.5	2.60; m
5β	5.05; br d; 1.9, 6.4	2.74; m; 3.4, 16.5	2.78; t; 6.5	2.81; m
9	2.92; ddd; 10.4, 8.0, 13.0	3.04; dd; 8.0, 13.1	—	—
10α	1.49; dd; 13.0, 13.2	1.64; dd; 13.0, 13.1	2.51; m	1.94; d; 14.8
10β	2.11; dd; 13.2, 8.0	1.98; dd; 13.0, 8.0	2.82; m	2.41; dd; 14.8, 1.9
12	1.42; s	1.31; s	—	—
13	1.75; s	1.65; s	2.07; s	2.02; s
14	3.38/3.31; d; 10.0	1.21; s	3.49; s	3.38; s
15	1.12; s	3.42; s	1.16; s	1.05; s

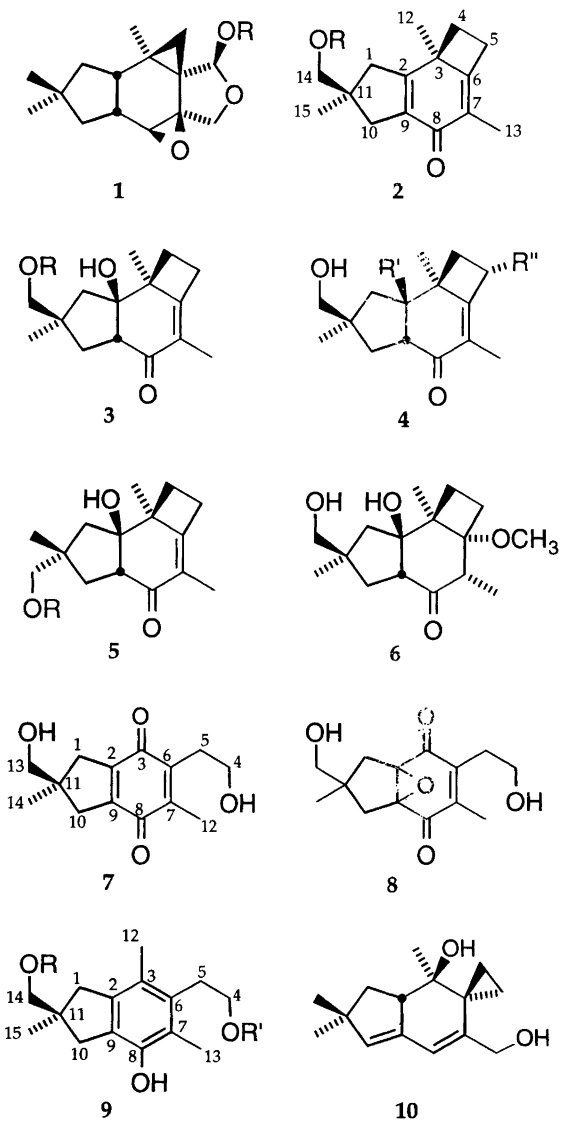

Fig. 1. a: R=R′=R″=H; b: R=stearoyl, R′=H, R″=OH; c: R=Ac, R′=R″=OH; d: R=H, R′=Ac; e: R=stearoyl, R′=Ac.

that it should be as presented in Fig. 1. The CD spectrum of **10** {$[\alpha]_D^{22} = +91°$ (*c* 0.4, MeOH)} showed a positive band at about 250 nm ($\Delta\varepsilon = +9.0\ cm^3\ mol^{-1}\ cm^{-1}$), associated with the longest wavelength π–π* transition of the transoid diene chromophore. Geometry optimization by the semiempirical MO-SCF AM1 method afforded (for the enantiomer shown in Fig. 1) the lowest energy conformer having a right-handed skewed diene moiety, the 7–8–9–10 dihedral angle being +163°. According to the skewed dienes helicity rule,[11] and taking into account that this feature is the predominant one, giving rise to the observed positive Cotton Effect,[12] it can be deduced that the stereochemistry shown also corresponds to the absolute configuration of **10**.

The structures of all new compounds were determined by NMR spectroscopy (including 2D COSY, NOESY, HMQC and HMBC experiments, although details are not given), and mass spectrometry. The absolute stereochemistry of plorantinone B (**3a**) has been shown to be as in Fig. 1,[8] the C-11 configuration of illudalane **9e** must be the same and it is reasonable to assume that this is also the case for deliquinone (**7**). 2,9-Epoxydeliquinone (**8**) is a minor product, and the possibility that its C-11 configuration is reversed, as in epiplorantinone B (**5a**), cannot be excluded. Compound **8** is also an exception in that it was not possible to determine the relative stereochemistry with the data from NOESY experiments. The 1D NMR data of the new natural products reported (**4b**, **5a**, **7** and **8**) are given in Tables 1 (^{1}H NMR data) and 2 (^{13}C NMR data).

Experimental

All solvents were distilled immediately before use. Fruit bodies of *Russula delica* Fr. were collected in the vicinity of Nanjing in P.R. China in the summer of 1997. They were brought on the same day to the laboratory and EtOAc and dichloromethane extracts were prepared as reported previously.[6,8] From 1 kg of fresh fruit bodies approximately 1.2 mg plorantinone D (**4b**), 15 mg epiplo-

Table 2. ^{13}C NMR data (δ; mult.) for plorantinone D (**4b**), epiplorantinone B (**5a**), deliquinone (**7**) and 2,9-epoxydeliquinone (**8**) in $CDCl_3$.

C	4b	5a	7	8
1	45.3; t	44.6; t	40.8; t	34.0; t
2	46.8; d	83.1; s	147.2; s	69.5; s
3	44.7; s	51.0; s	187.0; s	193.9; s
4	35.4; t	26.7; t	61.7; t	61.0; t
5	70.2; d	27.0; t	30.1; t	30.9; t
6	164.6; s	167.1; s	141.5; s	141.7; s
7	129.4; s	126.0; s	142.8; s	143.2; s
8	202.6; s	200.1; s	186.5; s	193.1; s
9	52.5; d	61.1; d	146.8; s	69.5; s
10	38.9; t	39.3; t	40.8; t	34.0; t
11	44.0; s	43.5; s	43.0; s	42.6; s
12	25.4; q	26.6; q	—	—
13	10.5; q	10.0; q	12.4; q	13.2; q
14	70.6; t	25.0; q	70.2; t	69.9; t
15	24.5; q	71.2; t	25.1; q	26.6; q

rantinone B (**5a**), 20 mg deliquinone (**7**) and 3 mg 2,9-epoxydeliquinone (**8**) was obtained. TLC analyses were carried out on Merck Kieselgel 60 F_{254} SiO_2 plates developed with MTBE–hexane mixtures and visualised by spraying with anisaldehyde–sulfuric acid and warming to 120 °C. HPLC was performed with 250 × 10 mm columns of both straight phase (MTBE–hexane mixtures), and on reversed phase (H_2O–CH_3CN mixtures). ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded at room temperature with a Bruker ARX500 spectrometer with an inverse multinuclear 5 mm probehead equipped with shielded gradient coil. The spectra were recorded for samples in $CDCl_3$ or C_6D_6 and the solvent signals (δ_H 7.26 and 7.16 ppm, δ_C 77.0 and 128.4 ppm, respectively) were used as references. The chemical shifts (δ) are given in ppm, and the coupling constants (J) in Hz. COSY, HMQC and HMBC experiments were recorded with gradient enhancements using sine shaped gradient pulses. For the 2D heteronuclear correlation spectroscopy the refocusing delays were optimised for $^1J_{CH} = 145$ Hz and $^nJ_{CH} = 10$ Hz. The raw data were transformed and the spectra were evaluated with standard Bruker UXNMR software (rev. 941001). Mass spectra were recorded with a Jeol SX102 spectrometer, while the UV and the IR spectra were recorded with a Varian Cary 2290 and a Perkin Elmer 298 spectrometer, respectively. Melting points (uncorrected) were determined with a Reichert microscope, and optical rotations were measured with a Perkin–Elmer 141 polarimeter at 22 °C.

14-O-Acetylplorantinone B (**3c**) was isolated as a colourless oil from the EtOAc extract of injured specimens. $[\alpha]_D^{22} = -5°$ (*c* 0.3, $CHCl_3$). EI-MS, *m/z* (% rel. int.): 292 (M^+, 24%), 250 (5), 122 (100), 94 (21), 79 (17), 69 (13), 43 (18). ^1H NMR (500 MHz, $CDCl_3$): δ 4.06 (1 H, d, $J_{14\alpha-14\beta} = 11.0$, 14-Hα), 4.01 (1 H, d, 14-Hβ), 3.02 (1 H, ddd, $J_{5\alpha-4a} = 10.0$, $J_{5\alpha-4b} = 9.0$, $J_{5\alpha-5\beta} = 12.4$, 5-Hα), 2.97 (1 H, dd, $J_{9-10\alpha} = 13.4$, $J_{9-10\beta} = 8.4$, 9-H), 2.76 (1 H, ddd, $J_{5\beta-4\beta} = 9.0$, $J_{5\beta-4\alpha} = 3.3$, 5-Hβ), 2.67 (1 H, ddd, $J_{4\alpha-4\beta} = 9.6$, 4-Hβ), 2.32 (1 H, dd, $J_{10\alpha-10\beta} = 13.5$, 10-Hβ), 2.09 (3 H, s, 2′-H_3), 2.03 (1 H, d, $J_{1\alpha-1\beta} = 15.2$, 1-Hα), 1.69 (1 H, dd, 4-Hα), 1.65 (3 H, s, 13-H_3), 1.60 (1 H, d, 1-Hβ), 1.50 (1 H, dd, 10-Hα), 1.33 (3 H, s, 12-H_3), 1.09 (3 H, s, 15-H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (C-8), 171.6 (C-1′), 166.9 (C-6), 125.9 (C-7), 83.1 (C-2), 71.4 (C-14), 62.0 (C-9), 50.4 (C-3), 45.4 (C-1), 41.7 (C-11), 39.9 (C-10), 27.0 (C-5), 26.7 (C-4), 26.5 (C-12), 25.2 (C-15), 21.2 (C-2′), 9.8 (C-13).

Plorantinone D (**4b**) was obtained as a colourless oil. $[\alpha]_D^{22} < \pm 1°$ (*c* 0.1 $CHCl_3$). EI-MS, *m/z* (% rel. int.): 250.1574 (M^+, 100 %, $C_{15}H_{22}O_3$ requires 250.1569), 219 (32), 203 (40), 189 (92), 175 (49), 173 (40), 159 (24), 135 (34), 122 (78), 109 (40), 95 (60), 81 (58), 79 (46), 55 (41), 43 (40), 41 (35). See Tables 1 and 2 for NMR data.

epi-*Plorantinone B* (**5a**) was obtained as white crystals, m.p. 126–129 °C ($CHCl_3$/hexane). $[\alpha]_D^{22} = +8°$ (*c* 0.4 in $CHCl_3$). EI-MS, *m/z* (% rel. int.): 250.1568 (M^+, 30%, $C_{15}H_{22}O_3$ requires 250.1569), 232 (3), 219 (8), 122 (100), 107 (17), 94 (26), 79 (29), 32 (28). See Tables 1 and 2 for NMR data.

Compound **6** was obtained as the only product from transesterification of stearoyldelicone **2b** (10 mg) by catalytic amounts of MeOK in MeOH (1 ml). After 1 h at room temperature the starting material was consumed, and the reaction solution was passed through an Al_2O_3 column. The eluate was concentrated and purified by RP HPLC, yielding 1.5 mg **6** as a white oil. $[\alpha]_D^{22} = +59°$ (*c* 0.15 in $CHCl_3$). EI-MS, *m/z* (% rel. int.): 292 (M^+, 24%), 250 (5), 122 (100), 94 (21), 79 (17), 69 (13), 43 (18). ^1H NMR (500 MHz, C_6D_6): δ 3.08 (2 H, m, 14-H_2), 2.92 (3 H, s, 1′-H_3), 2.71 (1 H, d, $J_{10\alpha-10\beta} = 16.1$, 10-Hα), 2.60 (1 H, d, $J_{7-13} = 7.1$, 7-H), 2.42 (1 H, d, 10-Hβ), 2.38 (1 H, d, $J_{1\alpha-1\beta} = 17.9$, 1-Hβ), 2.08 (1 H, d, 1-Hα), 1.90 (1 H, ddd, $J_{5\alpha-5\beta} = 11.8$, $J_{5\alpha-4\alpha} = 8.9$, $J_{5\alpha-4\beta} = 4.6$, 5-Hα), 1.82 (1 H, ddd, $J_{4\alpha-4\beta} = 10.5$, $J_{4\alpha-5\beta} = 7.2$, 4-Hα), 1.65 (1 H, ddd, $J_{5\beta-4\beta} = 8.6$, 5-Hβ), 1.51 (1 H, ddd, 4-Hβ), 1.26 (3 H, s, 12-H_3), 1.25 (3 H, d, 13-H_3), 1.00 (3 H, s, 15-H_3). ^{13}C NMR (125 MHz, C_6D_6): δ 198.5 (C-8), 163.7 (C-2), 133.8 (C-9), 83.2 (C-6), 70.3 (C-14), 50.4 (C-1′), 47.4 (C-7), 44.4 (C-3), 42.8 (C-1), 42.6 (C-11), 40.3 (C-10), 29.4 (C-4), 26.5 (C-5), 24.6 (C-15), 18.8 (C-12), 12.0 (C-13).

Deliquinone (**7**) was obtained as a yellow oil, $[\alpha]_D^{22} = -0.5°$ (*c* 0.6 in $CHCl_3$). UV λ_{max} (MeOH)/nm: 350 (ε/dm^3 mol^{-1} cm^{-1} 180), 273 (10 300). EI-MS, *m/z* (% rel. int.): 250.1205 (M^+, 100 %, $C_{14}H_{18}O_4$ requires 250.1206), 232 (8), 221 (61), 203 (56), 189 (28), 175 (30), 159 (23), 145 (18), 91 (21), 77 (18). See Tables 1 and 2 for NMR data.

2,9-Epoxydeliquinone (**8**) was obtained as a colourless oil, $[\alpha]_D^{22} < \pm 1°$ (*c* 0.1 $CHCl_3$). EI-MS, *m/z* (% rel. int.): 266.1153 (M^+, 10%, $C_{14}H_{18}O_5$ requires 266.1154), 248 (15), 237.1124 (100, $C_{13}H_{17}O_4$ requires 237.1127), 236

(37), 223 (34), 205 (44), 189 (58), 175 (77), 161 (47), 137 (72), 136 (89), 91 (49), 53 (52), 43 (46). See Tables 1 and 2 for NMR data.

Illudalane **9e** was formed in quantitative yields when 10 mg stearoyldelicone (**2b**) were dissolved in 25 ml EtOAc containing 1% acetic acid, and the solvent was evaporated off on a rotavapor at 35 °C. **9e** is a colourless oil, $[\alpha]_D^{22} = -1$ (*c* 4.5 in $CHCl_3$). UV λ_{max} (cyclohexane)/nm: 283 (ε/dm^3 mol^{-1} cm^{-1} 940), 225sh (6900), 203 (36 000). EI-MS, *m/z* (% rel. int.): 558 (M^+, 35%), 275 (33), 274 (100), 215 (52), 214 (71), 201 (59), 199 (47), 187 (33), 57 (17), 43 (33). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.11 (2 H, t, J_{4-5} = 8.0, 4-H), 4.01 (2 H, s, 14-H), 2.98 (2 H, t, 5-H), 2.87 (1 H, d, J_{1a-1b} = 15.9, 1-Ha), 2.86 (1 H, d, $J_{10a-10b}$ = 15.5, 10-Ha), 2.66 (1 H, d, 1-Hb), 2.62 (1 H, d, 10-Hb), 2.31 (2 H, t, $J_{2'-3'}$ = 7.5, 2′-H_2), 2.23 (3 H, s, 13-H_3), 2.16 (3 H, s, 12-H_3), 2.07 (3 H, s, 2″-H_3), 1.61 (2 H, quintet, 3′-H_2), 1.25 (28 H, br, 4′- to 17′-H_2), 1.19 (3 H, s, 15-H_3), 0.88 (3 H, t, 18′-H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6 (C-1′), 171.6 (C-1″), 148.8 (C-8), 140.6 (C-2), 133.9 (C-6), 125.4 (C-9), 125.3 (C-3), 121.4 (C-7), 71.6 (C-15), 63.7 (C-4), 43.4 (C-1), 43.2 (C-11), 40.0 (C-10), 34.8 (C-2′), 32.4 (C-3′), 30.1–29.8 (12 C, C-4′ to 15′), 29.7 (C-5), 25.4 (2 C, C-16′ and C-14), 23.1 (C-17′), 21.5 (C-2″), 16.1 (C-12), 14.6 (C-18′), 12.1 (C-13).

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