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Sesquiterpene constituents from the essential oils of the liverworts *Mylia taylorii* and *Mylia nuda*

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Abstract

The essential oils and extracts of *Mylia taylorii* and *M. nuda* were investigated by gas chromatography, mass spectrometry, NMR spectroscopy and chemical correlations. Beside several known compounds 13 new constituents including three new carbon skeletons could be identified. Four hydrocarbons with a molecular formula of $C_{15}H_{22}$ (m/z 202) were identified as myli-4(15)-ene (**1**), aromadendra-1(10),4(15)-diene (**19**), aromadendra-4,10(14)-diene (**20**) and aromadendra-4,9-diene (**21**). Three oxaspiro-compounds were identified as 7-*epi*-bourbon-3-en-5,11-oxide (**22**), guai-3,10(14)-dien-5,11-oxide (**23**) and guai-3,9-dien-5,11-oxide (**24**). The absolute configuration of myli-4(15)-en-3-one (**5**) could be established by chemical correlation. Together with α-taylorione (**7**) the corresponding 6,11-*seco*-compound taylopyran (**25**) with a new carbon skeleton was identified which serves as a precursor to taylocyclane (**26**) and taylofuran (**27**). Taynudol (**28**) contains a new carbon skeleton with a cyclobutenyl structure.

Keywords: *Mylia taylorii*; *Mylia nuda*; Liverworts; Sesquiterpenoids; Structure elucidation

1. Introduction

The liverwort *Mylia taylorii* (Hook.) S. Gray (Jungermanniaceae) is known as a rich source for unique sesquiterpenoids with rare skeletons like oxygenated *ent*-5,10-*cyclo*-aromadendranes (**3**, **4**) (myliane skeleton), *ent*-1,10-*seco*-aromadendranes (**6**, **8**) (tayloriane skeleton), myltaylanes (**9**) and cyclomyltaylanes (**12**) (Asakawa, 1995; Nagashima and Asakawa, 1998). Continuous investigations over the last 30 years, mainly by Matsuo and Takaoka, have resulted in the isolation and identification of (−)-myliol (**3**) (Benesova et al., 1971, 1973; Matsuo et al., 1976; Nozaki, 1979), (−)-taylorione (**6**) (Matsuo et al., 1974, 1979), (−)-dihydromylione A (**4**) (Matsuo et al., 1977), (−)-myltaylenol (**9**) (Takaoka et al., 1985), (+)-cyclomyltaylenol (**12**) (Takaoka et al., 1988), (−)-3-acetoxytaylorione (**8**), (+)-maali-4(15)-en-1β-ol (**14**), (+)-4(15)-dehydroglobulol (**15**), (+)-*ent*-globulol (**16**) and others (Matsuo and Takaoka, 1990) (Scheme 1). In addition, the dimeric sesquiterpenoids myltaylorione A (**33**), myltaylorione B (**34**) and bitaylorione (**35**) (Fig. 4) have been described (Takaoka et al., 1991). For the related *M. nuda* Inoue and Yang, which is endemic to Taiwan, the isolation of **3** and **4**, together with the unique nudenal (**17**) and nudenoic acid (**18**) (Liu et al., 1996; Wu, 1997), as well as labdane diterpenoids (Wu and Asakawa, 1987) were reported. In contrast to the former species, the related *M. anomala* and *M. verrucosa* are known to predominantly contain diterpenoids with the verrucosane skeleton (Asakawa, 1995; Nagashima and Asakawa, 1998).

In order to clarify the phytochemical relationship between the sesquiterpenoid bearing *M. taylorii* and *M. nuda* we investigated the essential oils and extracts of both species from different collection sites by GC-MS. Thirteen new compounds were isolated and identified by spectroscopic techniques and chemical correlations.

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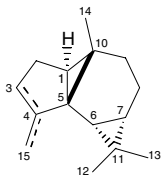
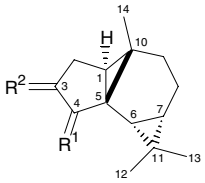
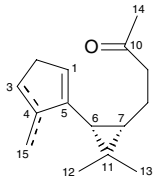


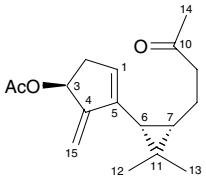
1: $\Delta^{4(15)}$
2: Δ^{3}



3: $R^1 = CH_2$; R^2 = OH, H (*3S*)
4: $R^1 = CH_3$, H (*4R*); R^2 = O
5: $R^1 = CH_2$; R^2 = O



6: $\Delta^{4(15)}$
7: Δ^{3}



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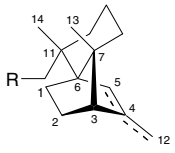
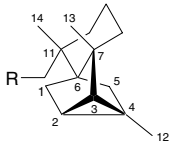
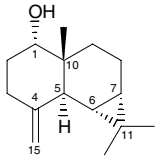


9: R = OH; $\Delta^{4(12)}$
10: R = H; $\Delta^{4(12)}$
11: R = H; Δ^{4}



12: R = OH
13: R = H



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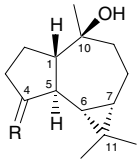
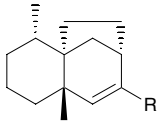


15: R = CH_2
16: R = CH_3, H (*4S*)



17: R = CHO
18: R = COOH

Scheme 1. Sesquiterpene constituents from *Mylia*.

2. Results and discussion

2.1. M. taylorii

M. taylorii was collected near Reutte, Tyrol, in the Austrian Alps. Hydrodistillation of the fresh plant material afforded a complex mixture of sesquiterpenoids. Several known constituents could be identified by comparison of their mass spectra and retention indices with a spectral library (Joulain and König, 1998; Hochmuth et al., 2003) established under identical experimental conditions (Table 1). The remaining unidentified components were selected for isolation by a combination of column chromatography and preparative thin-layer chromatography, as well as preparative and semi-preparative gas chromatography using different polysiloxane- and modified cyclodextrin columns. A total number of 30 compounds could be identified by one- and two-dimensional NMR spectroscopy as well as chemical correlations (Table 1). Isolated sesquiterpenoids considered to be specific for the *Myliioidae* include **3**, **4**, **6**, **8**, **9**, **12** and **14**. In addition to **9** and **12** the corresponding hydrocarbons **10** (Adio et al., 2002), **11** (Adio, 2004) and **13** (Wu and Chang, 1992) were also detected. Thirteen new sesquiterpene constituents (**1**, **5**, **7**, **19**–**28**) could be obtained, including four with previously unknown carbon skeletons (see Scheme 2).

2.1.1. (−)-(1R*,5S*,6R*,7S*,10S*)-Myli-4(15)-ene (1)

An early eluting hydrocarbon **1** with the molecular formula of $C_{15}H_{22}$ (*m*/*z* 202) was observed in very small quantity among the hydrodistillation products, while larger amounts of **1** could be isolated from *n*-hexane extracts by a combination of column chromatography and semi-preparative GC. The ^{1}H NMR spectrum of **1** exhibited an exocyclic methylene group at δ_H 5.09 (1H, *s*) and 5.12 (1H, *s*), in accordance to signals at 104.7 (*t*) and 156.7 (*s*) in the ^{13}C Pendant spectrum. In addition, three tertiary methyl groups at δ_H 0.99 (3H, *s*), 1.02 (3H, *s*) and 1.05 (3H, *s*), corresponding to carbon signals at δ_C 15.1 (*q*), 15.8 (*q*) and 30.7 (*q*), as well as one cyclopropyl methine proton at δ_H 0.53 (1H, *dt*) were identified. The ^{13}C Pendant and HMQC spectra indicated four methylene groups at δ_C 16.6 (*t*), 23.6 (*t*), 32.7 (*t*) and 34.7 (*t*), three methine groups at δ_C 20.1 (*d*), 22.6 (*d*), 34.9 (*d*) and three quaternary carbons at δ_C 18.6 (*s*), 22.8 (*s*) and 37.0 (*s*), which confirmed the presence of a cyclopropyl unit. Considering the molecular formula and one exocyclic double bond a tetracyclic system had to be assumed. The H,H correlations in the COSY spectrum exhibited the characteristic pattern of a 5,10-*cyclo*-aromadendrene, whose partial structures could be connected to a myli-4(15)-ene structure (**1**) by inspection of the HMBC spectrum. The relative configuration (*1R*,5S*,6R*,7S*,10S**) was derived from a NOESY spectrum, which exhibited NOEs between 6-H, 7-H and 12-H_3 on one side, and between 13-H_3 and 1-H on the other side of the molecule. **1** represents the exocyclic double bond isomer of the co-occurring (+)-anastreptene (**2**) which is widely distributed among the liverworts, but unknown from higher plants (Andersen et al., 1977, 1978; Asakawa, 1995).

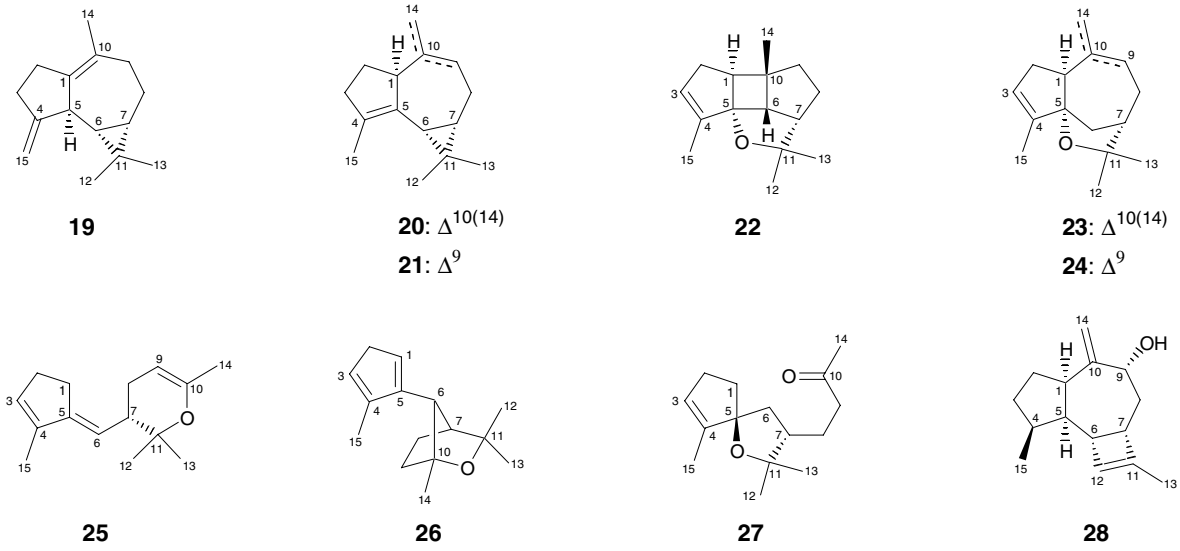
Table 1
Identified sesquiterpene constituents in *Mylia taylorii*, *Mylia nuda* and *Kurzia trichoclados* listed in their order of elution from the unpolar CPSil-5 column

Compound	*Mylia taylorii*			*Mylia nuda*		*Kurzia trichoclados*
	Austria	Germany	Canada	Taiwan	Taiwan	Austria
Cyclomyltaylane (**13**)	++ *	+	++			+
Anastreptene (**2**)	+ *	+	++	++	+	++
Myltayl-4-ene (11)	+		+			+
β-Elemene	+	+	+	+	+	
α-Barbatene	+	+	+			+
Tritomarene	+	+	+	+	+	+
Myli-4(15)-ene (1)	+ *	+	++	+	+	
Bourbon-11-ene	+	+	+	+	+	+
γ-Maaliene	+			+	+	
Aromadendra-4,10(14)-diene (20)	+ *	+	+	++	+	
Isobazzanene	+++ *	++	+++			+
Aromadendrene	+		+	+		
β-Barbatene	+		+			+++
Myltayl-4(12)-ene (**10**)	++ *	+	++			+
Aromadendra-1(10),4-diene (**30**)	+ *	+	+	++	+	+
allo-Aromadendrene	+	+	+	+	+	++
7-*epi*-Bourbon-3-en-5,11-oxide (22)	+++ *	+		+++ *	+	++
β-Chamigrene	++	+	++			+
Taylocyclane (26)	+ *			+	+	
Germacrene D	+	+	+	+	+	
Ledene				+++ *	+	+++
ent-Bicyclogermacrene	++ *	+	++	+ *	+	
β-Himachalene	+	+				
α-Chamigrene	+		++			
Aromadendra-1(10),4(15)-diene (19)	+++ *	++	+	++	++	+
Guai-3,9-dien-5,11-oxide (24)	+ *			+		
β-Bazzanene	+		+			
γ-Cuprenene	+		+			
Aromadendra-4,9-diene (21)	+ *			++		+
Taylopyran (25)	+++ *	++	+	+++	++	+
δ-Cuprenene	+	+	+			
Guai-3,10(14)-dien-5,11-oxide (23)	+ *			+		
Spathulenol	+		++			+
4-Dehydroviridiflorol (**29**)	+++ *	++	++	+++	+	+++
ent-Globulol (**16**)	++ *	++	+	++	+	++
4(15)-Dehydroglobulol (**15**)	++ *	+	+ *	++		
Dihydromylione A (**4**)	+++ *	+	+	+++ *	+	+
α-Taylorione (7)	++ *	+++		++	++	
Rosifoliol	+			+	+	+
Myliol (**3**)	+++ *	+++	+++	++ *	+++	+
Taylorione (**6**)	++ *	++	+++ *	+	+	+
Myli-4(15)-en-3-one (5)	++ *	++	+	+++ *	+	
Maali-4(15)-en-1-ol (**14**)	++ *	++	+	+++	+	+
Cyclomyltaylenol (**12**)	+++ *	+++	+++			++
Taylofuran (27)	++ *	+		++	+	
Taynudol (28)	+ *	+		+		
Myltaylenol (**9**)	+ *	+	+			
3-Acetoxytaylorione (**8**)			+++ *			
Additional sesquiterpene constituents	+	+	++	+	++	+++

Bold letters designate new compounds; +, ++, +++ represent relative concentrations; *, identified by NMR spectroscopy.

2.1.2. (+)-(5S,6S*,7S*)-Aromadendra-1(10),4(15)-diene (**19**)*

Another hydrocarbon with a molecular formula of $C_{15}H_{22}$ (*m/z* 202) was observed as a major constituent in the hydrodistillation products. However, in *n*-hexane extracts rich in **1** the amount of **19** was comparatively low, suggesting the presence of a rearrangement product of the highly labile myli-4(15)-ene (**1**). From the essential oil the isolation of **19** was achieved by column chromatography and preparative GC. The ^{1}H NMR



Scheme 2. New sesquiterpene constituents from *Mylia*.

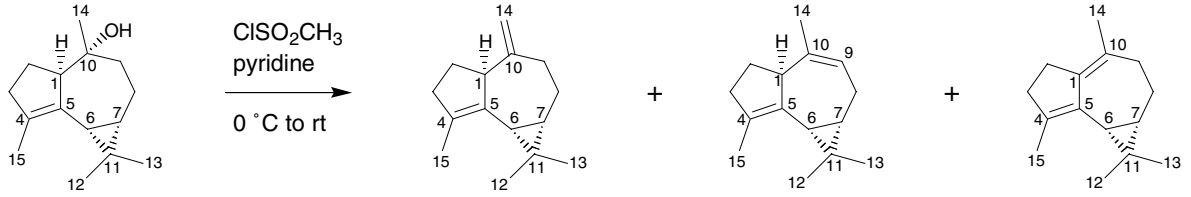
spectrum showed signals for one exocyclic methylene group at δ_H 4.92 (1H, *s*,*br*) and 5.02 (1H, *d*,*br*) in agreement with carbon signals at δ_C 104.9 (*t*) and 158.2 (*s*) in the ^{13}C Pendant spectrum which also indicated an internal double bond at δ_C 126.8 (*s*) and 137.3 (*s*). One broad singlet signal at δ_H 1.54 (3H, *s*,*br*) could be attributed to an olefinic methyl group, which, together with two tertiary methyl groups at δ_H 1.05 (3H, *s*) and 1.12 (3H, *s*), corresponded to carbon signals at δ_C 16.0 (*q*), 22.0 (*q*) and 29.1 (*q*). In addition, two cyclopropyl methine protons at δ_H 0.59 (1H, *m*) and 0.89 (1H, *dd*) and one allylic methine group at δ_H 3.04 (1H, *d*,*br*) could be identified. The ^{13}C Pendant and HMQC spectra indicated the presence of four methylene groups at δ_C 23.6 (*t*), 31.8 (*t*), 32.9 (*t*), 37.0 (*t*), three methine groups at δ_C 26.9 (*d*), 35.2 (*d*), 42.7 (*d*) and one quaternary cyclopropyl carbon at δ_C 19.1 (*s*). Inspection of the COSY spectrum indicated an ethylene bridge adjacent to three consecutive methine groups, with two of them being part of the cyclopropyl ring with a geminal dimethyl substitution. Together with the remaining ethylene bridge which exhibited a single multiplet signal in the ^1H NMR spectrum and lacked any cross peaks in the COSY spectrum, the two partial structures could be connected according to their HMBC correlations to reveal an aromadendra-1(10),4(15)-diene structure (**19**). The relative configuration was obtained from a NOESY spectrum which exhibited NOEs between the methyl group 12-H_3 and both cyclopropyl methine protons 6-H and 7-H, indicating a (*Z*)-fused cyclopropyl ring. The adjacent methyl group 13-H_3 on the opposite side of the molecule exhibited a NOE with the allylic methine proton 5-H, leading to the relative configuration of a (*5S*,6S*,7S**)-aromadendra-1(10),4(15)-diene (**19**).

*2.1.3. (+)-(1S,6R,7S)-Aromadendra-4,10(14)-diene (**20**)*

Although **20** co-elutes with isobazzanene on various stationary phases, separation could be achieved by preparative GC with two different cyclodextrin columns. The ^1H NMR spectrum exhibited an exocyclic methylene group at δ_H 5.01 (2H, *s*,*br*), in agreement with carbon signals at δ_C 108.0 (*t*) and 150.4 (*s*) in the ^{13}C NMR spectra, which also indicated an internal double bond at δ_C 136.1 (*s*) and 137.9 (*s*). One olefinic methyl group at δ_H 1.65 (3H, *s*,*br*) and two tertiary methyl groups at δ_H 0.87 (3H, *s*) and 1.08 (3H, *s*) corresponded to carbon signals at δ_C 15.1 (*q*), 16.7 (*q*), 29.0 (*q*). Furthermore, one allylic methine group at δ_H 3.07 (1H, *s*,*br*) could be identified. Inspection of COSY and HMQC spectra allowed the construction of a consecutive partial structure that could be connected to afford **20** in agreement with the long-range COSY, HMBC and NOESY correlations. The absolute configuration of **20** was determined by a chemical correlation with (+)-dehydroviridiflorol (**29**) of known absolute configuration (Warmers et al., 1998) as shown in Fig. 1.

*2.1.4. (1S,6R,7S)-Aromadendra-4,9-diene (**21**)*

The ^1H NMR spectrum of **21** is similar to **20** but exhibited an olefinic proton at δ_H 5.73 (1H, *t*,*br*) in agreement with signals for an endocyclic double bond at δ_C 124.2 (*d*) and 138.8 (*s*) in the ^{13}C NMR spectra which also indicated another internal double bond at δ_C 131.7 (*s*) and 135.4 (*s*). Two olefinic methyl groups at δ_H 1.69 (3H, *d*) and 1.72 (3H, *d*) and two tertiary methyl groups at δ_H 0.96 (3H, *s*) and 1.09 (3H, *s*) corresponded to carbon signals at δ_C 14.9 (*q*), 16.7 (*q*), 21.4 (*q*) and 29.4 (*q*). The resulting structure and relative configuration of **21** is in agreement with the COSY, HMBC and NOESY spectra. In addition to **20** and **21** the corresponding



29 **20** **21** **30**

Fig. 1. Dehydration of (+)-4-dehydroviridiflorol (**29**).

double bond isomer (−)-(*6R,7S*)-aromadendra-1(10),4-diene (**30**), previously described (without stereochemical information) from *Myroxylon balsamum*, Fabaceae (Friedel and Matusch, 1987), was obtained. **30** was also detected as the major dehydration product of the co-occurring (+)-4-dehydroviridiflorol (**29**) together with small amounts of (**20**) and (**21**) (Fig. 1). GC-MS investigations of various liverworts have shown **20**, **21** and **30** to be prominent in *Diplophyllum plicatum*, *D. albicans* and *Barbilophozia* species (König et al., 2003).

2.1.5. (−)-(1S,5S*,6S*,7S*,10S*)-7-epi-Bourbon-3-en-5,11-oxide (**22**)*

As a major constituent of the essential oil of *M. taylorii* **22** was isolated from an early polar fraction by preparative GC. HRMS afforded the molecular formula $C_{15}H_{22}O$. The ^1H NMR spectrum allowed the identification of one olefinic proton at δ_H 5.42 (1H, *s*) in agreement with an endocyclic double bond at δ_C 128.8 (*d*) and 141.71 (*s*) in the ^{13}C Pendant spectrum. One olefinic methyl group at δ_H 1.74 (3H, *d*) and three tertiary methyl groups at δ_H 0.95 (3H, *s*), 1.10 (3H, *s*) and 1.33 (3H, *s*) corresponded with carbon signals at δ_C 12.3 (*q*), 19.9 (*q*), 24.1 (*q*) and 31.3 (*q*). Furthermore the ^{13}C Pendant spectrum indicated three methylene groups at δ_C 27.5 (*t*), 31.9 (*t*) and 43.9 (*t*), three methine groups at δ_C 48.2 (*d*), 54.3 (*d*) and 58.5 (*d*) together with three quaternary carbons at δ_C 39.8 (*s*), 85.8 (*s*) and 91.7 (*s*). Considering the molecular formula a tetracyclic compound was assumed, while the chemical shifts of two quaternary carbons pointed towards the presence of an oxacyclic substructure.

The COSY spectrum allowed the identification of two partial structures together with a geminal dimethyl group derived from intensive ^4J-W-H,H-correlations. From the HMBC spectrum the location of these methyl groups adjacent to the oxacyclic ring was clarified. Additional correlations provided the connectivities of the three quaternary carbons to reveal a bourbon-3-en-5,11-oxide structure (**22**). The 1,10-(*E*)-fusion of the bourbonane skeleton was evident from the ^4J-W-H,H-correlation between 1-H and the methyl group 14-H_3 in the COSY spectrum and the spatial interaction between 1-H and 9-H in a NOESY spectrum. Additional NOEs between 14-H_3 and 6-H indicated the 6,10-(*Z*)-fusion. The relative configurations at C-5 and C-7 were derived from NOEs between the olefinic methyl group 15-H_3, the methine proton 6-H, the tertiary methyl group 12-H_3 and the methine proton 7-H on one side of the molecule and between the remaining methyl group 13-H_3 and the methine proton 1-H on the opposite side of the molecule. **22** represents the first oxacyclic sesquiterpenoid with the bourbonane skeleton and exhibits the formerly unknown 7-*epi*-configuration.

2.1.6. (+)-(1S,5S*,7S*)-Guai-3,10(14)-dien-5,11-oxide (**23**)*

The first polar fraction afforded two oxacyclic sesquiterpenoids (**23**, **24**) present as minor constituents, which could be isolated by preparative GC. HRMS established a molecular formula of $C_{15}H_{22}O$. The ^1H NMR spectrum of **23** exhibited signals for one olefinic proton at δ_H 5.34 (1H, *s*,*br*) and one exocyclic methylene group at δ_H 4.81 (1H, *t*) and 4.91 (1H, *s*,*br*), in agreement with an endocyclic double bond at δ_C 124.4 (*d*) and 144.2 (*s*) and an exocyclic double bond at δ_C 110.9 (*t*) and 151.8 (*s*) in the ^{13}C NMR spectra. One olefinic methyl group at δ_H 1.73 (3H, *m*) and two tertiary methyl groups at δ_H 1.10 (3H, *s*) and 1.30 (3H, *s*) corresponded to carbon signals at δ_C 12.9 (*q*), 23.5 (*q*) and 31.3 (*q*). In addition, one allylic methine group at δ_H 3.04 (1H, *dd*) could be identified, whereas the ^{13}C NMR and HMQC spectra indicated four methylene groups at δ_C 31.7 (*t*), 32.5 (*t*), 34.7 (*t*), 35.1 (*t*), two methine groups at δ_C 45.6 (*d*) and 58.7 (*d*) and two quaternary carbons at δ_C 82.3 (*s*) and 94.9 (*s*). Considering the molecular formula and the two identified double bonds a tricyclic structure could be expected, while the chemical shifts of the quaternary carbons implied an oxacyclic substructure. By inspection of the COSY spectrum a consecutive partial structure was elucidated, which could be connected with the remaining two quaternary carbons according to their HMBC correlations to give a guai-3,10(14)-diene-5,11-oxide structure (**23**). The relative configuration was derived from a NOESY spectrum. NOEs between the olefinic methyl group 15-H_3, a methylene bridge proton 6-H_1, one tertiary methyl group 12-H_3 and the bridgehead proton 7-H indicated the location of these protons on the same side of the molecule. The remaining methyl group 13-H_3 on the

opposite side exhibited a NOE with an allylic methylene proton 9-H_1 which again showed a NOE with the allylic methine proton 1-H, thus establishing the relative configuration of **23** to be a (*1S*,5S*,7S**)-guai-3,10(14)-dien-5,11-oxide.

2.1.7. (−)-(1S,5S*,7S*)-Guai-3,9-dien-5,11-oxide (**24**)*

The ^{1}H NMR spectrum of **24** was similar to **23** but exhibited two olefinic protons at δ_H 5.17 (1H, *s*,*br*) and 5.34 (1H, *s*,*br*) in agreement with two endocyclic double bonds at δ_C 120.6 (*d*), 123.3 (*d*), 135.0 (*s*) and 145.9 (*s*) in the ^{13}C Pendant spectrum. Two olefinic methyl groups at δ_H 1.63 (3H, *d*) and 1.77 (3H, *t*) together with two tertiary methyl groups at δ_H 1.18 (3H, s) and 1.32 (3H, *s*) corresponded to carbon signals at δ_C 11.8 (*q*), 25.7 (*q*), 26.2 (*q*) and 31.6 (*q*). In addition one allylic methine group at δ_H 2.85 (1H, *t*,*br*) could be identified. The resulting structure of a guai-3,9-dien-5,11-oxide **24** is in agreement with the COSY and HMBC correlations. Although the stereochemistry at 5-C and 7-C was evident from the NOESY spectrum, an unambiguous relative configuration for 1-C could not be derived due to missing correlations. The relative configuration of **24** was therefore determined by a chemical correlation with **23** (Fig. 2). Upon palladium catalysed hydrogenation **23** and **24** gave the same guai-3-en-5,11-oxide (**31**) and guaiaoxide (**32**) identified by GC-MS, which implied the relative configuration at 1-C of **23** and **24** to be identical. While various guai-5,11-oxides are known from higher plants (Hirota et al., 1975, 1980; Oyedeji et al., 1998), their occurrence among the liverworts has not been reported previously.

*2.1.8. (−)-(1S,5R,6R,7S,10S)-Myli-4(15)-en-3-one (**5**)*

In addition to **3**, **4** and the corresponding hydrocarbons **1** and **2**, another oxygenated *ent*-5,10-*cyclo*-aromadendrane type compound with a molecular ion signal at *m*/*z* 216 (**5**) could be identified. Co-eluting together with **4** during column chromatographic prefractionation, **5** could be isolated by preparative GC. HRMS afforded a molecular formula of $C_{15}H_{20}O$. In the ^{1}H NMR spectrum two olefinic protons at δ_H 5.09 (1H, *s*) and 6.28 (1H, *s*) were identified, which corresponded to an exocyclic double bond at δ_C 115.2 (*t*) and 149.7 (*s*) in conjugation to a carbonyl group at δ_C 204.7 (*s*) in the ^{13}C NMR spectra. In addition, three tertiary methyl groups at δ_H 0.72 (3H, *s*), 0.88 (3H, *s*) and 0.97 (3H, *s*), in agreement with carbon signals at δ_C 14.9 (*q*), 15.2 (*q*) and 30.6 (*q*), could be identified. Three cyclopropyl methine protons at δ_H 0.51 (1H, *dt*), 0.98 (1H, *d*) and 1.28 (1H, *d*) corresponded to signals at δ_C 20.5 (*d*), 22.1 (*d*), 25.8 (*d*) in the ^{13}C NMR and HMQC spectra which also indicated three additional methylene groups at δ_C 16.1 (*t*), 31.9 (*t*) and 37.0 (*t*) and three quaternary carbons at δ_C 19.2 (*s*), 25.5 (*s*) and 33.0 (*s*). Considering the molecular formula, a tetracyclic skeleton had to be assumed. Inspection of the COSY spectrum revealed a close similarity to the 5,10-*cyclo*-aromadendranes and together with the HMBC spectrum structure **5** could be identified. Its relative configuration was established from a NOESY spectrum, while the absolute configuration was determined by chemical correlation (Fig. 3) with **3** and **4** of known absolute configuration (Matsuo et al., 1976, 1977; Nozaki, 1979). **5** has already been proposed as a natural precursor for the dimeric myltayloriones **33** and **34** (Fig. 4) (Asakawa, 1995).

2.1.9. (−)-(6R,7S)-α-Taylorione (7)

In addition to taylorione (**6**) a second constituent (**7**) with a similar mass spectrum was detected in the essential oil of *M. taylorii*. The isolation of **7** was troublesome, because it partially rearranged to **6** during preparative gas chromatography. Therefore, **7** was enriched by repeated column chromatography and finally isolated by preparative thin-layer chromatography. The ^{1}H and ^{13}C NMR spectra of **7** were similar to **6** and

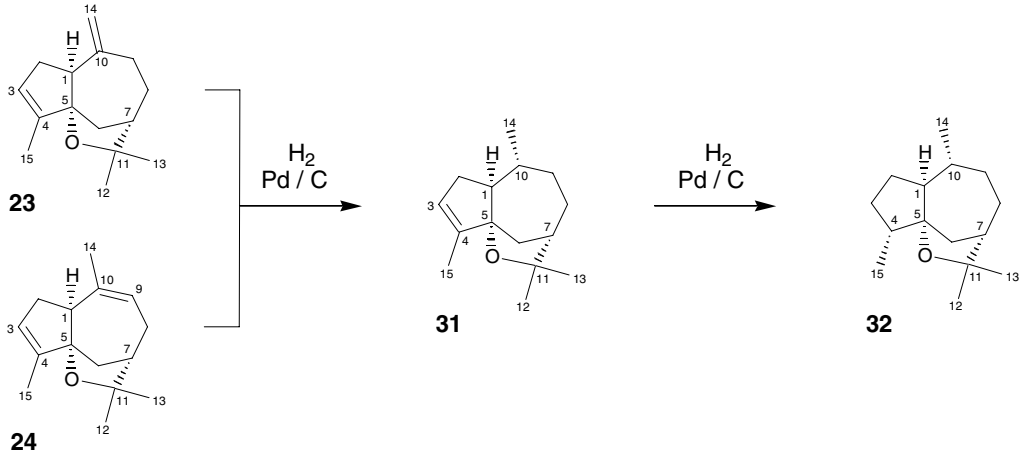


Fig. 2. Chemical correlation of the guaidien-5,11-oxides (**23**,**24**).

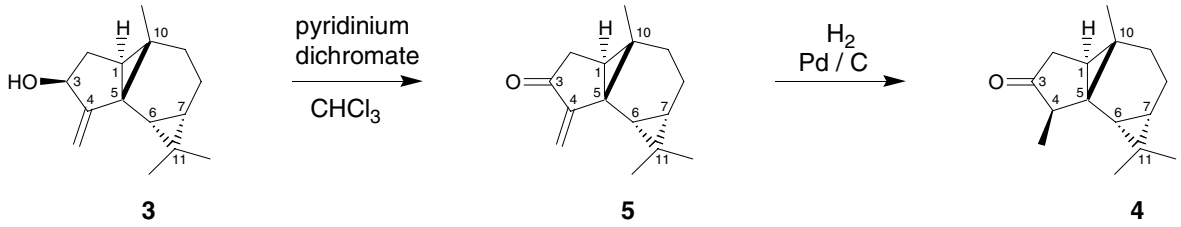


Fig. 3. Chemical correlation of (−)-myli-4(15)-en-3-one (**5**) with (−)-myliol (**3**) and (−)-dihydromylione A (**4**).

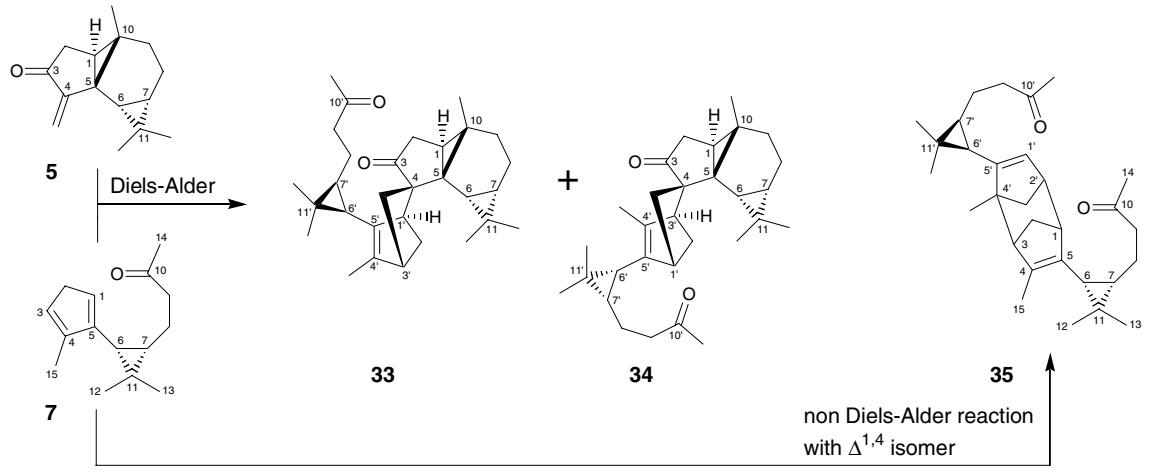


Fig. 4. Proposed biogenesis of dimeric myltayloriones (**33**,**34**) by Diels–Alder addition between **5** and **7**.

exhibited signals for a (*Z*)-fused geminal dimethyl cyclopropyl unit and a methyl group adjacent to a carbonyl group. Within the cyclopentyl moiety, however, two olefinic protons at δ_H 6.01 (1H, *s*,*br*) and 6.04 (1H, *s*,*br*) and one olefinic methyl group at δ_H 1.95 (3H, *d*) were identified, in agreement with the assignment of two endocyclic double bonds at δ_C 127.3 (*d*), 127.7 (*d*), 136.6 (*s*) and 144.5 (*s*) in the ^{13}C NMR spectra, respectively. These data implied a taylori-1(5),3-dien-10-one structure called α-taylorione (**7**), which was also supported by the COSY and HMBC spectra. Compound **7**, together with **5**, has already been proposed as a natural precursor for the dimeric myltayloriones **33** and **34** which are their Diels–Alder adducts, while the identification of bitaylorione (**35**) indicates the presence of additional unidentified double bond isomers with tayloriane skeleton (Fig. 4) (Takaoka et al., 1991; Asakawa, 1995). In order to establish the absolute configuration of **7** we investigated the acid catalysed rearrangement of (−)-(*6R,7S*)-taylorione (**6**) with known stereochemistry (Matsuo et al., 1979; Nakayama et al., 1979) utilizing the acidic ion exchange resin amberlyst® 15. In addition to some unknown compounds (−)-(*6R,7S*)-α-taylorione (**7**), identical to the natural product, could be identified (Fig. 5).

*2.1.10. (−)-(7S)-(E)-Taylopyran (**25**)*

In addition to **7** a large quantity of an unknown compound **25** with a molecular ion signal at *m*/*z* 218 and

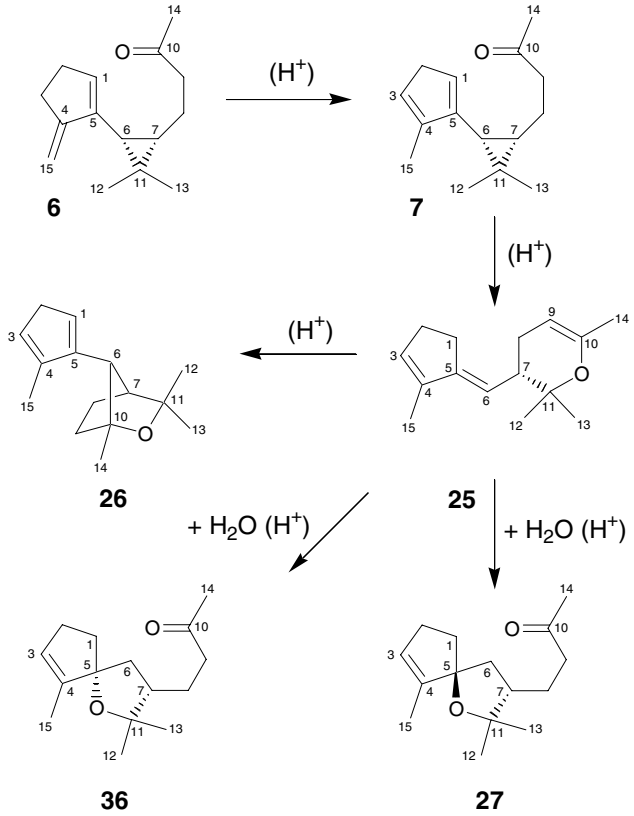


Fig. 5. Chemical correlation and proposed biogenetic pathway from **6** via **7** and **25** to **26**, **27** and **36**.

a predominating base peak at m/z 148 was detected among the acid catalysed rearrangement products of **6**, which was also present in the essential oils of *M. taylorii* and *M. nuda*. Upon chromatographic prefractionation **25** appeared to be highly polar when eluting after the sesquiterpene alcohols, although its GC retention time was comparatively low. While **25** was stable to isolation by preparative GC using polysiloxane SE-30, complete decomposition to a large number of unknown compounds was observed upon storage at elevated temperatures and even at 7 °C in benzene. HRMS confirmed the molecular formula $C_{15}H_{22}O$. From the ^1H NMR spectrum two olefinic protons at δ_H 5.12 (1H, *d*) and 5.62 (1H, *s*) were identified in agreement with carbon signals for two endocyclic double bonds at δ_C 118.2 (*d*), 133.9 (*d*), 140.6 (*s*) and 148.8 (*s*). The observed chemical shifts of a methine group at δ_H 4.50 (1H, *s,br*) and δ_C 93.9 (*d*), together with two quaternary carbons at δ_C 76.8 (*s*) and 149.2 (*s*), indicated the presence of an enolether moiety and consequently a bicyclic system had to be assumed. In addition, two olefinic methyl groups at δ_H 1.68 (3H, *d*) and 1.81 (3H, *s,br*) and two tertiary methyl groups at δ_H 1.23 (3H, *s*) and 1.34 (3H, *s*) were identified which corresponded to carbon signals at δ_C 13.1 (*q*), 21.0 (*q*), 21.3 (*q*) and 28.0 (*q*). Furthermore, the remaining two allylic methylene groups at δ_H 2.21 (2H, *m*) and 2.41 (2H, *m*), as well as one anisochoric methylene group with the geminal coupling constant $^2J = 17.0$ Hz at δ_H 1.91 (1H, *ddt*) and 2.11 (1H, *d,br*) adjacent to a stereogenic methine group at δ_H 2.48 (1H, *dt*) could be identified, in agreement with the assignment of the ^{13}C Pendant signals at δ_C 26.5 (*t*), 27.9 (*t*), 30.4 (*t*) and 42.7 (*d*). The COSY spectrum allowed the construction of two partial structures, whereas a geminal dimethyl group was evident from ^4J-W-H,H-correlations. Inspection of the HMBC spectrum confirmed the location of these methyl groups adjacent to the quaternary carbon of the enolether. The resulting structure of **25** is in accordance with the predominance of the corresponding Retro-Diels–Alder fragment ion $[M–H_2C{=}CHCO{-}CH_3]^+$ at m/z 148 as shown by HRMS. The new carbon skeleton of **25** represents a 6,11-*seco*-taylori-3,5,9-trien-10,11-oxide structure which we called taylopyran. The (*E*)-configuration was derived from spatial interactions between the olefinic methine proton 6-H and the cyclopentenyl methyl group 15-H_3 and between the methine proton of the dihydropyran unit 7-H and the methylene protons of the cyclopentenyl fragment 1-H_2 in the NOESY spectrum (Fig. 6). Additional NOEs indicated the presence of at least two conformers for **25**. NOEs between 8-$H_{(Si)}$,12-$H_{3(Re)}$ and 6-H, as well as 13-$H_{3(Si)}$ and 1-H are specific for an equatorial conformation at 7-C, while NOEs between 8-$H_{(Re)}$ and 13-$H_{3(Si)}$ as well as 12-$H_{3(Re)}$, 7-H and 1-H are specific for an axial conformation at 7-C. The (*E*)-configuration of **25** corresponds to the preferred conformation of the presumed precursors **6** and **7**, as shown by inspection of their NOESY spectra in combination with semi-empirical molecular modelling using MOPAC. The absolute configuration of **25** was derived from the identity of the natural product with (−)-(*7S*)-(*E*)-taylopyran obtained by rearrangement of (−)-(*6R,7S*)-taylorione (**6**) with known absolute configuration (Matsuo et al., 1979; Nakayama et al., 1979) (Fig. 5). The dihydropyran substructure of **25** readily added alcohols under acidic conditions to form diastereomeric mixtures of acetals and is believed to react reversibly with free hydroxyl functions of the silica gel, thus explaining the very low retention factor observed during column chromatography.

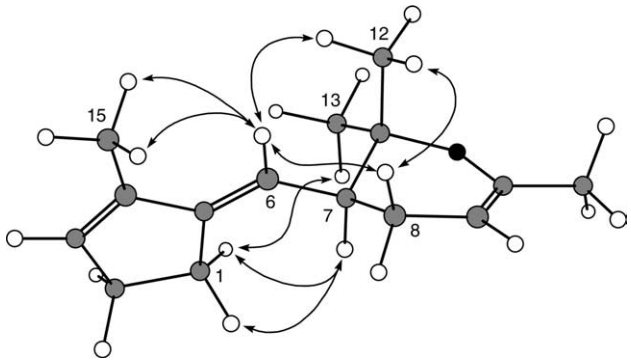


Fig. 6. Molecular model (AM1,MOPAC) of (−)-**25** with relevant NOEs.

2.1.11. (−)-(6S,7S,10R)-Taylocyclane (*26*)

Among the acid catalysed rearrangement products of **6** another constituent, called taylocyclane (**26**), with a similar mass spectrum to **6** and **7**, was detected by GC-MS. **26** was also present in small quantities (about 1% of the total volatiles) among the hydrodistillation products of *M. taylorii* and could be isolated from a slightly polar fraction by preparative GC. HRMS afforded the molecular formula $C_{15}H_{22}O$. The ^1H and ^{13}C NMR spectra exhibited some similarities with **7**, as far as the methylcyclopentadienyl moiety is concerned, but lacked any evidence for a cyclopropyl substructure or a carbonyl group. In the ^1H NMR spectrum two olefinic methine protons at δ_H 5.89 (1H, *s*) and 6.00 (1H, *s*) were identified in agreement with the assignment of two endocyclic double bonds at δ_C 127.0 (*d*), 128.1 (*d*), 143.7 (*s*) and 144.3 (*s*). One olefinic methyl group at δ_H 1.91 (3H, *s*) and three tertiary methyl groups at δ_H 1.24 (3H, *s*), 1.25 (3H, *s*) and 1.47 (3H, *s*) corresponded to carbon signals at δ_C 14.6 (*q*), 19.0 (*q*), 26.3 (*q*) and 29.7 (*q*). In addition, one methine proton at δ_H 3.00 (1H, *s,br*) could be identified in the ^1H NMR spectrum, whereas the ^{13}C Pendant and HMQC spectra indicated the presence of three methylene groups at δ_C 23.3 (*t*), 34.2 (*t*) and 39.9 (*t*), two methine groups at δ_C 51.2 (*d*) and 52.4 (*d*) and two quaternary carbons at δ_C 78.0 (*s*), 86.5 (*s*). Con-

sidering the five units of unsaturation for the molecular formula $C_{15}H_{22}O$ a tricyclic system was assumed, while the chemical shifts of the two quaternary carbons confirmed the presence of an oxacyclic substructure. Inspection of the COSY spectrum revealed two adjacent methine groups with a connectivity to an ethylene bridge. The resulting partial structures were connected according to their HMBC correlations to reveal a new carbon skeleton with a 6,11-*seco*-6,10-*cyclo*-tayloridien-10,11-oxide structure (**26**), that was named taylocyclane. The relative configuration (*6S*,7S*,10R**) was derived from the ^4J-W-H,H-coupling correlations between the axial protons of the ethylene bridge 8-H_{ax} and 9-H_{ax} and the allylic methine proton 6-H in the COSY spectrum, in agreement with spatial interactions between 6-H and the equatorial methyl group 12-H_3 and between the olefinic proton 1-H, an equatorial proton of the ethylene bridge 9-H_{eq} and the bridgehead methyl group 14-H_3 in the NOESY spectrum (Fig. 7). **26** most likely originates from cyclisation of **25**, present in part as the axial conformer, which fulfils the stereochemical requirements (Fig. 5).

2.1.12. (5S*,7S*)-Taylofuran (27)

In addition to **7**, **25** and **26** another sesquiterpenoid (**27**) was detected in small quantities among the rearrangement products of **6**, which was also present in the essential oil of *Mylia* and could be isolated from an alcohol fraction by repeated column chromatography and semi-preparative GC. Surprisingly the mass spectrum of **27** exhibited a molecular ion signal at *m/z* 236 and was attributed the molecular formula $C_{15}H_{24}O_2$ by HRMS. The ^{1}H NMR spectrum displayed one olefinic methine proton at δ_H 5.40 (1H, *s,br*) in agreement with an endocyclic double bond at δ_C 126.6 (*d*), 143.4 (*s*) in the ^{13}C Pendant spectrum. Two tertiary methyl groups at δ_H 0.98 (3H, *s*), 1.27 (3H, *s*), one olefinic methyl group at δ_H 1.72 (3H, *d*) and one methyl group at 1.68 (3H, *s*), adjacent to a carbonyl group at δ_C 205.7 (*s*), corresponded to carbon signals at δ_C 12.0 (*q*), 24.3 (*q*), 29.4 (*q*) and 29.9 (*q*), respectively. In addition, the ^{13}C Pendant and HMQC spectra indicated five methylene groups at δ_C 24.0 (*t*), 29.0 (*t*), 39.7 (*t*), 41.0 (*t*), 42.8 (*t*), one methine group at δ_C 48.7 (*d*) and two quaternary carbons at δ_C 81.6 (*s*) and 92.9 (*s*). That led to the molecular formula $C_{15}H_{24}O$ and confirmed that **27** is not an alcohol. Considering the four units of unsaturation, the identification of one C,C– and one C,O– double bond implied a bicyclic structure, while the chemical shifts of the quaternary carbons indicated the presence of an oxacyclic substructure. From the COSY spectrum two partial structures could be identified. HMBC correlations provided the connectivities of the quaternary carbons to reveal an oxaspiro compound with a 6,11-*seco*-taylori-3-en-10-on-5,11-oxide structure (**27**) called taylofuran. **27** can be considered as a hydration product of **25** by addition of water to the enolether group and cleavage of the pyran ring under formation of the carbonyl group followed by an acid catalysed cyclisation of the resulting intermediate. The relative configuration (*5S*,7S**) was derived from careful inspection of a NOESY spectrum. A second compound with identical mass spectrum was also detected by GC-MS and most likely represents the diastereomeric (*5R*,7S**)-taylofuran (**36**) (Fig. 5). Considering the probable artificial nature of **7**, **25**, **26** and **27** we investigated *n*-hexane, dichloromethane, diethyl ether and methanol extracts of crushed and intact *M. taylorii* and *M. nuda* plant material by GC-MS and were able to identify the questionable components as well. The mild isolation conditions applied support the authentic presence of these compounds as natural constituents of *M. taylorii* and *M. nuda*.

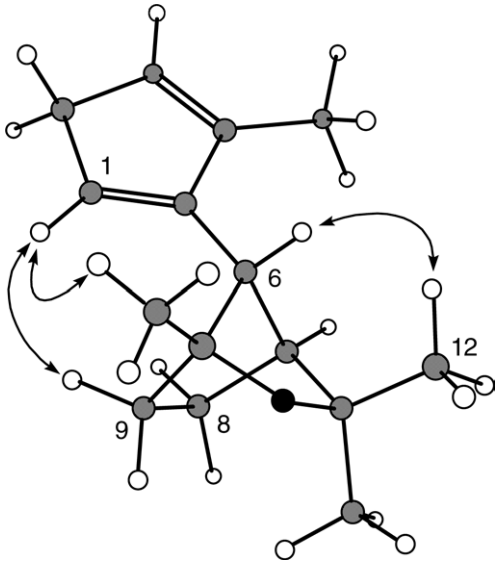


Fig. 7. Molecular model (AM1,MOPAC) of (−)-**26** with relevant NOEs.

2.1.13. (1R*,4S*,5S*,6R*,7S*,9R*)-Taynudol (28)

From an enriched alcohol fraction the tricyclic taynudol with a 2,5,8-trimethyl-decahydro-cyclobuta-[*e*]azulene skeleton (**28**) was obtained by a combination of repeated column chromatography and semi-preparative GC. By HRMS the molecular formula $C_{15}H_{22}O$ was established. From the ^{1}H NMR spectrum one olefinic methine proton at δ_H 5.76 (1H, *s,br*) and two exocyclic methylene protons at δ_H 4.81 (1H, *s,br*) and 4.83 (1H, *s,br*) were identified, which corresponded to an endocyclic double bond with carbon signals at δ_C 132.3 (*d*) and 147.6 (*s*) and an exocyclic double bond with absorptions at δ_C 111.4 (*t*) and 153.7 (*s*) in the ^{13}C Pendant spectrum. In addition, one olefinic methyl group at δ_H 1.49 (3H, *d*) and one secondary methyl group at δ_H 0.93 (3H, *d*, $J = 7.3$ Hz) could be identified

in agreement with carbon signals at δ_C 14.3 (*q*) and 17.2 (*q*). Furthermore, the ^{1}H NMR spectrum exhibited a methine proton at δ_H 4.03 (1H, *dd*) which corresponded to a hydroxy methine group at δ_C 77.2 (*d*), as well as two characteristic broad doublet signals at δ_H 2.48 (1H, *d*,*br*) and 2.55 (1H, *d*,*br*). The ^{13}C Pendant and HMQC spectra indicated five methine groups at δ_C 38.2 (*d*), 41.2 (*d*), 41.6 (*d*), δ_C 44.1 (*d*), 45.3 (*d*) and additional three methylene groups at δ_C 28.3 (*t*), 32.7 (*t*) and 33.6 (*t*). All together these CH-fragments added up to the molecular formula $C_{15}H_{21}$ which supported the presence of a tricyclic sesquiterpene alcohol. The observation of only one exocyclic methylene and two methyl groups strongly suggested an unusual skeleton and from the coupling correlations of COSY and HMBC spectra the new 2,8-dimethyl-5-methylene-2a,3,4,5,5a,6,7,8,8a,8b-decahydro-cyclobuta[*e*]azulen-4-ol structure, called taynudol (**28**), could be identified. The cyclobutenyl moiety was evident from the long-range coupling correlations between the olefinic methyl group 13-H_3 and both cyclobutenyl methine protons 6-H, 7-H, while the olefinic cyclobutenyl proton 12-H lacked any coupling correlation except with 13-H_3. The position of the olefinic methyl group was consequently confirmed by the HMBC correlations to 7-C. The observed chemical shifts and coupling constants within the cyclobutenyl moiety are in agreement with reported values (Bernart et al., 1993). The (*Z*)-configuration of the cyclobutenyl ring was evident on the basis of the vicinal coupling constants of $J = 13.9$ Hz (6-H, *d*,*br*) and $J = 12.3$ Hz (7-H, *d*,*br*) (Bernart et al., 1993) and could be confirmed by the spatial interaction between 5-H und 8-H_{Re} in the NOESY spectrum (Fig. 8). Additional NOEs, observed between 6-H, 15-H_3, 2-H_{Re} and 14-H_E, as well as NOEs between 14-H_Z, 9-H and 7-H indicated a (*Z*)-decahydroazulene configuration in (*1R*,4S*,5S*,6R*,7S*, 9R**)-taynudol (**28**). The new carbon skeleton of **28** most likely originates from a guai-11-enyl-6-carbenium ion.

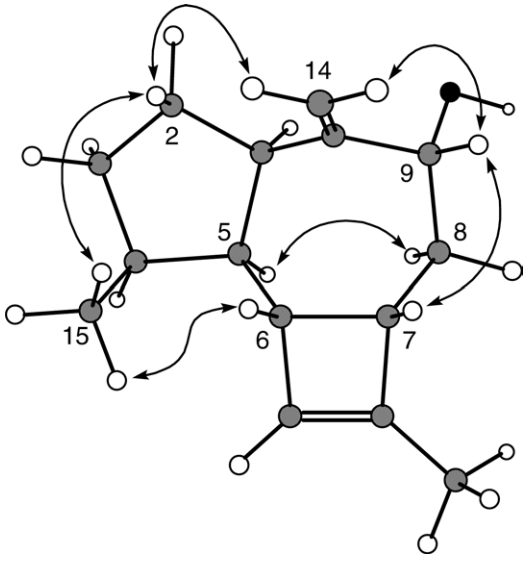


Fig. 8. Molecular model (AM1, MOPAC) of (−)-**28** with relevant NOEs.

2.2. *M. nuda*

M. nuda was collected near Yuen-yang lake, Ilan county (Taiwan). Hydrodistillation of the fresh plant material afforded a complex sesquiterpenoid mixture with similar constituents as *M. taylorii* (Table 1). This high similarity in essential oil composition was confirmed by a comprehensive GC-MS investigation of *M. taylorii* samples from the Austrian Alps (Tyrol), German Alps (Allgäu) and Jervis Inlet (Canada), together with samples of *M. nuda* from Yuen-yang lake and Taiping Shan (Taiwan) (Table 1).

Nudenal (**17**) and nudenoic acid (**18**), previously considered as specific markers for *M. nuda* (Asakawa, 1995, Nagashima and Asakawa, 1998), could not be detected, while labdane diterpenoids were identified in varying amounts in additional samples of both *M. taylorii* and *M. nuda* from Yuen-yang lake and Taiping Shan (Taiwan) (data not shown). **8** was only present in Canadian *M. taylorii*. Beside quantitative differences in essential oil composition all the *M. nuda* samples investigated were found to lack barbatene-, isobazzanene-, chamigrene-, cuprenene-, myltaylene- and cyclomyltaylane-type compounds (Table 1). A variety of sesquiterpenoids formerly believed to be specific markers for the *Myliioidae* like **3**, **4**, **6**, **12** and **14**, as well as the new **22** and **25** were also detected in the essential oil of *Kurzia trichoclados*, Lepidoziaceae (Table 1).

3. Experimental

3.1. General experimental procedures

3.1.1. GC, GC-MS and GC-HRMS

Gas chromatograms were run using a Carlo Erba HRGC 5300 Mega instrument equipped with 25 m fused silica capillary columns with polysiloxanes CPSil-5 and CPSil-19 (Chrompack) or Carlo Erba Fractovap 2150 or 4160 instruments equipped with 25 m fused silica capillary columns with octakis-(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin or heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin in OV-1701 (1:1; w/w). Hydrogen at 0.5 bar inlet pressure was used as carrier gas. Split injection at 200 °C (split ratio: 1:30); flame ionisation detector at 250 °C. Temp. progr. 50–230 °C at 3 °C/min. Electron impact (70 eV) GC-MS and GC-HRMS measurements were carried out on a Hewlett Packard HP 5890 gas chromatograph equipped

with a 25 m CPSil-5 CB (Chrompack) fused silica capillary column coupled to a VG Analytical 70-250S mass spectrometer.

3.1.2. NMR spectroscopy

NMR measurements were carried out with a Bruker WM 400 instrument for ^{1}H NMR (400.1 MHz), broadband decoupled ^{13}C NMR and ^{13}C Pendant spectra (100.6 MHz) and with WM 500 instrument for ^{1}H NMR, COSY, HMQC, HMBC and *gp*-NOESY spectra (^{1}H: 500.1 MHz, ^{13}C: 125.8 MHz). Benzene-d_6 was used as solvent and TMS served as internal standard.

3.1.3. Polarimetry

Measurements were performed with a polarimeter 341 (Perkin–Elmer) at 589 nm and 20 °C. Due to the small amounts of isolated compounds only the sense of optical rotation could be determined.

3.1.4. Preparative GC

Preparative GC was carried out with a modified Varian 1400 gas chromatograph equipped with a stainless steel column (1.85 m×4.3 mm; Silcosteel, Amchro) with 10% SE 30 on Chromosorb W-HP, 15% SE 52 on Chromosorb W-HP, 5% octakis-(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin in OV-1701 (1:1; w/w) on Chromosorb W-HP, or 6.4% heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin in SE-52 (1:1; w/w) on Chromosorb W-HP. Helium was used as carrier gas at a flow rate of approximately 120 ml/min. Injector and detector (FID) temperatures were 200 and 250 °C, respectively. Eluting fractions were trapped in Teflon tubes cooled with liquid nitrogen (Hardt and König, 1994).

3.1.5. Semi-preparative GC

Semi-preparative GC was carried out with a HP 6890 gas chromatograph equipped with an autosampler and a megabore thickfilm capillary column (30 m, i.d. 0.53 mm, film thickness 5 μm) with polysiloxane DB-1 or DB-1701. Helium was used as carrier gas. Injector and detector (FID) temperatures were 200 and 250 °C, respectively. Eluting fractions were trapped at −20 °C in glass tubes using the automatic fraction collector PFC 1 from Gerstel, Mülheim, Germany, and a cryostat.

3.2. Plant material, essential oils and extracts

Plant material of *M. taylorii* (Hook.) S. Gray was collected in October 2002 and in April 2003 near Reutte, Tyrol (Austria), in December 1994 near Walserschanz, Allgäu (Germany) and in 1999 at Jervis Inlet (Canada). Plant material of *M. nuda* Inoue and Yang was collected in March 1998 at Yuen-yang Lake, Hsinchu Hsien and Taiping Shan (Taiwan). Plant material of *K. trichoclados* was collected in 2003 near Zillertal (Austria). The liverworts were identified by H. Muhle (Universität Ulm). The carefully cleaned fresh plant material was homogenated in water with a blender and submitted to hydrodistillation for 2.5 h to yield the essential oil which was collected in *n*-hexane. Alternatively, air dried plant material was extracted with organic solvents at 7 °C (*n*-hexane, dichloromethane, diethyl ether, methanol) or powdered under liquid nitrogen prior to extraction.

3.3. Isolation of single compounds

After prefractionation of the raw essential oils and enrichment of the constituents by repeated column chromatography with silica 60 F_{254} (Merck) and a pentane–diethyl ether gradient or *n*-hexane–ethyl acetate mixture (8/1), respectively, the compounds were isolated by a combination of preparative TLC using glass plates with silica 60 F_{254} (Merck) with different solvent systems, preparative GC using polysiloxane SE-30, SE-52, octakis-(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin or heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin columns and semi-preparative GC using thickfilm capillary columns with DB-1 or DB-1701.

3.4. (−)-(1R,5S*,6R*,7S*,10S*)-Myli-4(15)-ene (**1**)*

1,1,3a-Trimethyl-6-methylene-1,1a,2,3,3a,3b,4,5,6,6b-decahydrocyclopenta[2,3]cyclopropa-[1,2-*a*]cyclopropa[*c*]-benzene. Colorless oil; sense of optical rotation (benzene): (−); $RI_{CPSil-5}$ 1419; ^{1}H NMR (500.1 MHz, C_6D_6) $\delta = 0.53$ (1H, *dt*, $J = 8.8$ Hz, $J = 9.2$ Hz, 7-H), 0.72 (1H, *m*, 8-H_{Si}), 0.99 (3H, *s*, 14-H), 1.02 (3H, *s*, 12-H_{Si}), 1.05 (3H, *s*, 13-H_{Re}), 1.22 (1H, *d*, $J = 9.5$ Hz, 6-H), 1.44 - 1.53 (4H, *m*, 1-H, 2-H, 9-H, 9-H′), 1.62 (1H, *m*, 8-H_{Re}), 1.85 (1H, *m*, 2-H′), 2.16 (1H, *m*, 3-H_{Si}), 2.51 (1H, *t*,*br*, $J = 14.7$ Hz, 3-H_{Re}), 5.09 (1H, *s*, 15-H_E), 5.12 (1H, *s*, 15-H_Z); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 15.1$ (*q*, 12-$C_{(Si)}$), 15.8 (*q*, 14-C), 16.6 (*t*, 8-C), 18.6 (*s*, 11-C), 20.1 (*d*, 7-C), 22.6 (*d*, 6-C), 22.8 (*s*, 5-C), 23.6 (*t*, 2-C), 30.7 (*q*, 13-$C_{(Re)}$), 32.7 (*t*, 9-C), 34.7 (*t*, 3-C), 34.9 (*d*, 1-C), 37.0 (*s*, 10-C), 104.7 (*t*, 15-C), 156.7 (*s*, 4-C); MS (EI, 70 eV) *m*/*z* (rel. int.): 202 (29) $[M]^+$, 187 (35), 173 (4), 159 (89), 145 (49), 131 (77), 117 (55), 105 (74), 91 (93), 77 (48), 65 (29), 53 (37), 41 (100).

3.5. (+)-(5S,6S*,7S*)-Aromadendra-1(10),4(15)-diene (**19**)*

1,1,4-Trimethyl-7-methylene-1a,2,3,5,6,7,7a,7b-octahydro-1*H*-cyclopropa[*e*]azulene. Colorless oil; sense of optical rotation (benzene): (+); $RI_{CPSil-5}$ 1510; ^{1}H NMR (500.1 MHz, C_6D_6) $\delta = 0.59$ (1H, *m*, 7-H), 0.89 (1H, *dd*, $J_1 = J_2 = 5.6$ Hz, 6-H), 1.05 (3H, *s*, 12-H_{Re}), 1.12 (3H, *s*, 13-H_{Si}), 1.51 (1H, *m*, 8-H_{Si}), 1.54 (3H, *s*,*br*, 14-H), 1.70 (1H, *m*, 8-H_{Re}), 2.10 (1H, *d*,*br*, $J = 18.0$ Hz, 9-H_{Re}), 2.21

(1H, *d,br*, $J = 4.2$ Hz, 9-H_{Si}), 2.30 (4H, *m*, 2-H, 3-H), 3.04 (1H, *d.br*, $J = 3.0$ Hz, 5-H), 4.92 (1H, *s,br*, 15-H_Z), 5.02 (1H, *d,br*, $J = 1.3$ Hz, 15-H_E); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 16.0$ (*q*, 13-$C_{(Si)}$), 19.1 (*s*, 11-C), 22.0 (*q*, 14-C), 23.6 (*t*, 8-C), 26.9 (*d*, 7-C), 29.1 (*q*, 12-$C_{(Re)}$), 31.8, 32.9 (2*t*, 2-C, 3-C), 35.2 (*d*, 6-C), 37.0 (*t*, 9-C), 42.7 (*d*, 5-C), 104.9 (*t*, 15-C), 125.8 (*s*, 10-C), 137.3 (*s*, 1-C), 158.2 (*s*, 4-C); MS (EI, 70 eV) *m/z* (rel. int.): 202 (27) $[M]^+$, 187 (9), 173 (1), 159 (42), 145 (11), 133 (100), 117 (17), 105 (53), 91 (58), 77 (24), 65 (12), 55 (19), 41 (54).

3.6. (+)-(1S,6R,7S)-Aromadendra-4,10(14)-diene (**20**)

1,1,7-Trimethyl-4-methylene-1a,2,3,4,4a,5,6,7b-octahydro-1*H*-cyclopropa[*e*]azulene. Colorless oil; sense of optical rotation (benzene): (+); $RI_{CPSil\text{-}5}$ 1440; ^{1}H NMR (500.1 MHz, C_6D_6) $\delta = 0.74$ (1H, *m*, 7-H), 0.87 (3H, *s*, 12-H_{Si}), 1.08 (3H, *s*, 13-H_{Re}), 1.11 (1H, *d,br*, 6-H), 1.27 (1H, *m*, 8-H_{Si}), 1.65 (3H, *s,br*, 15-H), 1.77 (1H, *m*, 8-H_{Re}), 1.89 (1H, *m*, 2-H_{Re}), 2.01 (1H, *m*, 2-H_{Si}), 2.15 (1H, *dd*, $J = 15.1$ Hz, $J = 8.8$ Hz, 3-H), 2.30 (1H, *m*, 3-H), 2.44 (1H, *d,br*, $J = 13.2$ Hz, 9-H_{Re}), 2.49 (1H, *m*, 9-H_{Si}), 3.07 (1H, *s,br*, 1-H), 5.01 (2H, *s,br*, 14-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 15.1$ (*q*, 15-C), 16.7 (*q*, 12-$C_{(Si)}$), 20.1 (*s*, 11-C), 21.4 (*t*, 8-C), 24.7 (*d*, 6-C), 27.6 (*d*, 7-C), 29.0 (*q*, 13-$C_{(Re)}$), 29.3 (*t*, 2-C), 36.4 (*t*, 3-C), 36.4 (*t*, 9-C), 50.7 (*d*, 1-C), 108.0 (*t*, 14-C), 136.1 (*s*, 4-C), 137.9 (*s*, 5-C), 150.4 (*s*, 10-C); MS (EI, 70 eV) *m/z* (rel. int.) : 202 (59) $[M]^+$, 187 (46), 173 (9), 159 (87), 145 (57), 131 (100), 117 (39), 105 (38), 91 (49), 77 (29), 65 (15), 53 (20), 41 (55).

3.7. (1S,6R,7S)-Aromadendra-4,9-diene (**21**)

1,1,4,7-Tetramethyl-1a,2,4a,5,6,7b-hexahydro-1*H*-cyclopropa[*e*]azulene. Colorless oil; sense of optical rotation: (*n.d.*); $RI_{CPSil\text{-}5}$ 1533; ^{1}H NMR (500.1 MHz, C_6D_6) $\delta = 0.95$ (1H, *m*, 7-H), 0.96 (3H, *s*, 12-H_{Si}), 1.09 (3H, *s*, 13-H_{Re}), 1.19 (1H, *d,br*, $J = 8.8$ Hz, 6-H), 1.69 (3H, *d*, $J = 0.9$ Hz, 15-H), 1.72 (3H, *d*, $J = 1.0$ Hz, 14-H), 1.88 (2H, *m*, 3-H), 2.03 (1H, *m*, 8-H_{Re}), 2.20–2.26 (3H, *m*, 2-H, 8-H_{Si}), 3.38 (1H, *s,br*, 1-H), 5.73 (1H, *t,br*, $J = 7.6$ Hz, 9-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 14.9$ (*q*, 15-C), 16.7 (*q*, 12-$C_{(Si)}$), 21.4 (*q*, 14-C), 21.9 (*s*, 11-C), 22.9 (*t*, 8-C), 25.0 (*d*, 6-C), 26.6 (*d*, 7-C), 26.9 (*t*, 2-C), 29.4 (*q*, 13-$C_{(Re)}$), 37.1 (*t*, 3-C), 50.2 (*d*, 1-C), 124.2 (*d*, 9-C), 131.7 (*s*, 5-C), 135.4 (*s*, 4-C), 138.8 (*s*, 10-C); MS (EI, 70 eV) *m/z* (rel. int.) : 202 (83) $[M]^+$, 187 (35), 173 (12), 159 (100), 145 (47), 131 (50), 117 (20), 105 (38), 91 (30), 77 (20), 65 (10), 53 (13), 41 (33).

3.8. Dehydration of (+)-4-dehydroviridiflorol (**29**)

A solution of 100 μg (+)-4-dehydroviridiflorol (**29**) (isolated from *M. taylorii*) in 500 μl *n*-hexane was treated with 200 μl pyridine and 100 μl methanesulfonyl chloride at 0 °C. After 4 h at room temperature the solution was washed with 1 ml water, dried over sodium sulphate and chromatographed on silica gel (*n*-hexane) to give **20**, **21** and **30**.

3.9. (−)-(1S*,5S*,6S*,7S*,10S*)-Bourbon-3-en-5,11-oxide (**22**)

Colorless oil; sense of optical rotation (benzene): (−); $RI_{CPSil\text{-}5}$ 1471; ^{1}H NMR (500.1 MHz, C_6D_6) $\delta = 0.95$ (3H, *s*, 14-H), 1.10 (3H, *s*, 12-H_{Re}), 1.33 (3H, *s*, 13-H_{Si}), 1.38 (1H, *dt*, $J = 6.9$ Hz, $J = 12.6$ Hz, 9-H_{Si}), 1.52 (1H, *dd*, $^2J = 12.0$ Hz, $J = 6.6$ Hz, 9-H_{Re}), 1.65 (1H, *dt*, $J = 13.2$ Hz, $J = 7.9$ Hz, 8-H_{Re}), 1.74 (3H, *d*, $J = 1.3$ Hz, 15-H), 2.02 (1H, *ddt*, $J = 9.5$ Hz, $J = 6.6$ Hz, $J = 12.9$ Hz, 8-H_{Si}), 2.10 (1H, *d,br*, $^2J = 17.3$ Hz, 2-H_{Re}), 2.17 (1H, *d*, $J = 10.1$ Hz, 1-H), 2.19 (1H, *t*, $J = 8.5$ Hz, 7-H), 2.44 (1H, *ddt*, $^2J = 17.3$ Hz, $J = 9.2$ Hz, $J = 2.2$ Hz, 2-H_{Si}), 2.54 (1H, *d*, $J = 7.9$ Hz, 6-H), 5.42 (1H, *s*, 3-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 12.3$ (*q*, 15-C), 19.9 (*q*, 14-C), 24.1 (*q*, 13-$C_{(Si)}$), 27.5 (*t*, 8-C), 31.3 (*q*, 12-$C_{(Re)}$), 31.9 (*t*, 2-C), 39.8 (*s*, 10-C), 43.9 (*t*, 9-C), 48.2 (*d*, 1-C), 54.3 (*d*, 7-C), 58.5 (*d*, 6-C), 85.8 (*s*, 11-C), 91.7 (*s*, 5-C), 128.8 (*d*, 3-C), 141.7 (*s*, 4-C); MS (EI, 70 eV) *m/z* (rel. int.) : 218 (96) $[M]^+$, 203 (30), 189 (4), 175 (22), 161 (23), 145 (21), 136 (66), 123 (100), 107 (30), 91 (30), 81 (31), 67 (18), 55 (19), 41 (53); HRMS $m/z = 218.1681$ $[M]^+$ (calc. for $C_{15}H_{22}O$: 218.1671).

3.10. (+)-(1S*,5S*,7S*)-Guai-3,10(14)-dien-5,11-oxide (**23**)

2,2,9-Trimethyl-6-methylene-3,4,5,6,6a,7-hexahydro-2*H*-3,9a-methanocyclopent[*b*]oxocine. Colorless oil; sense of optical rotation (benzene): (+); $RI_{CPSil\text{-}5}$ 1554; ^{1}H NMR (500.1 MHz, C_6D_6) $\delta = 1.10$ (3H, *s*, 12-H_{Re}), 1.30 (3H, *s*, 13-H_{Si}), 1.36 (1H, *m*, 8-H_{Re}), 1.70 (2H, *m*, 6-H_{Re}, 7-H), 1.73 (3H, *m*, 15-H), 1.78 (1H, *m*, 8-H_{Si}), 1.92 (1H, *ddd*, $^2J = 12.8$ Hz, $J = 7.1$ Hz, $J = 1.1$ Hz, 6-H_{Si}), 2.19 (2H, *m*, 2-H), 2.29 (1H, *ddd*, $J = 12.9$ Hz, $J = J = 4.1$ Hz, 9-H_{Si}), 2.59 (1H, *ddd*, $J = J = 13.2$ Hz, $J = 4.1$ Hz, 9-H_{Re}), 3.04 (1H, *dd*, $J = J = 8.4$ Hz, 1-H), 4.81 (1H, *t*, $J = 2.1$ Hz, 14-H_Z), 4.91 (1H, *s,br*, 14-H_E), 5.34 (1H, *s,br*, 3-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 12.9$ (*q*, 15-C), 23.5 (*q*, 13-$C_{(Si)}$), 31.3 (*q*, 12-$C_{(Re)}$), 31.7 (*t*, 2-C), 32.5 (*t*, 8-C), 34.7 (*t*, 9-C), 35.1 (*t*, 6-C), 45.6 (*d*, 7-C), 58.7 (*d*, 1-C), 82.3 (*s*, 11-C), 94.9 (*s*, 5-C), 110.9 (*t*, 14-C), 124.4 (*d*, 3-C), 144.2 (*s*, 4-C), 151.8 (*s*, 10-C); MS (EI, 70 eV) *m/z* (rel. int.) : 218 (98) $[M]^+$, 203 (49), 189 (33), 175 (28), 160 (30), 145 (53), 131 (29), 123 (42), 105 (46), 91 (71), 77 (48), 67 (26), 53 (38), 41 (100); HRMS $m/z = 218.1692$ $[M]^+$ ($C_{15}H_{22}O$; required: 218.1671).

3.11. (−)-(1S*,5S*,7S*)-Guai-3,9-dien-5,11-oxide (**24**)

2,2,6,9-Tetramethyl-3,4,6a,7-tetrahydro-2*H*-3,9a-methanocyclopent[*b*]oxocine. Colorless oil; sense of optical

rotation (benzene): (−); $RI_{CPSil\text{-}5}$ 1518; ^1H NMR (500.1 MHz, C_6D_6) $\delta = 1.18$ (3H, *s*, 12-H_{Re}), 1.32 (3H, *s*, 13-H_{Si}), 1.63 (3H, *d*, $J = 1.3$ Hz, 14-H), 1.77 (3H, *t*, $J = 1.2$ Hz, 15-H), 1.81 (2H, *m*, 2-H_{Si}, 7-H), 1.87 (1H, *d*, $J = 12.3$ Hz, 6-H_{Re}), 1.95 (1H, *dd*, $J = 11.9$ Hz, $J = 8.4$ Hz, 6-H_{Si}), 2.06 (1H, *m*, 8-H_{Re}), 2.22 (1H, *m*, 8-H_{Si}), 2.35 (1H, *m*, 2-H_{Re}), 2.85 (1H, *t*,*br*, $J = 8.6$ Hz, 1-H), 5.17 (1H, *s*,*br*, 9-H), 5.34 (1H, *s*,*br*, 3-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 11.8$ (*q*, 15-C), 25.7 (*q*, 13-$C_{(Si)}$), 26.2 (*q*, 14-C), 31.6 (*q*, 12-$C_{(Re)}$), 32.7 (*t*, 8-C), 33.9 (*t*, 6-C), 34.8 (*t*, 2-C), 44.6 (*d*, 7-C), 57.2 (*d*, 1-C), 83.0 (*s*, 11-C), 94.3 (*s*, 5-C), 120.6 (*d*, 9-C), 123.3 (*d*, 3-C), 135.0 (*s*, 10-C), 145.9 (*s*, 4-C); MS (EI, 70 eV) *m*/*z* (rel. int.) : 218 (21) $[M]^+$, 203 (13), 200 (31), 185 (17), 175 (27), 157 (53), 150 (41), 145 (44), 135 (30), 120 (100), 105 (42), 91 (39), 77 (27), 65 (12), 53 (19), 41 (44).

3.12. Hydrogenation of guaidien-5,11-oxides (*23*, *24*)

A solution of 100 μg **23** or **24** in 500 μl *n*-hexane was treated with 100 μg Pd/C (10%) and hydrogen bubbled through the solution for 10 min. After 2 h the solution was filtered and investigated by GC and GC-MS.

3.13. (−)-(1S,5R,6R,7S,10S)-Myli-4(15)-en-3-one (*5*)

1,1,3a-Trimethyl-6-methylene-5-oxo-1,1a,2,3,3a,3b,4,-5,6,6b-decahydrocyclopenta[2,3]cyclopropa[1,2-*a*]cyclopropa[*c*]benzene. Colorless oil; sense of optical rotation (benzene): (−); $RI_{CPSil\text{-}5}$ 1617; ^1H NMR (500.1 MHz, C_6D_6) $\delta = 0.51$ (1H, *dt*, $J = 8.8$ Hz, $J = 9.2$ Hz, 7-H), 0.60 (1H, *m*, 8-H_{Si}), 0.72 (3H, *s*, 14-H), 0.88 (3H, *s*, 12-H_{Si}), 0.97 (3H, *s*, 13-H_{Re}), 0.98 (1H, *d*, $J = n.d.$, 6-H), 1.28 (1H, *d*, $J = 6.6$ Hz, 1-H), 1.35 (2H, *m*, 9-H), 1.55 (1H, *m*, 8-H_{Re}), 2.11 (1H, *d*, $^2J = 19.6$ Hz, 2-H), 2.28 (1H, *dd*, $^2J = 19.6$ Hz, $^2J = 6.3$ Hz, 2-H′), 5.09 (1H, *s*, 15-H_Z), 6.28 (1H, *s*, 15-H_E); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 14.9$ (*q*, 12-$C_{(Si)}$), 15.2 (*q*, 14-C), 16.1 (*t*, 8-C), 19.2 (*s*, 11-C), 20.5 (*d*, 7-C), 22.1 (*d*, 6-C), 25.5 (*s*, 10-C), 25.8 (*d*, 1-C), 30.6 (*q*, 13-$C_{(Re)}$), 31.9 (*t*, 9-C), 33.0 (*s*, 5-C), 37.0 (*t*, 2-C), 115.2 (*t*, 15-C), 149.7 (*s*, 4-C), 204.7 (*s*, 3-C); MS (EI, 70 eV) *m*/*z* (rel. int.) : 216 (73) $[M]^+$, 201 (42), 188 (7), 173 (100), 160 (30), 159 (30), 145 (76), 131 (52), 117 (48), 105 (58), 91 (72), 77 (42), 69 (33), 53 (33), 41 (74); HRMS $m/z = 216.1515$ $[M]^+$ (calc. for $C_{15}H_{20}O$: 216.1514).

3.14. Partial synthesis of (−)-myli-4(15)-en-3-one (*5*)

A solution of 2 mg (−)-myliol (**3**) isolated from *M. taylorii* in 1 ml trichloromethane was treated with 50 mg molecular sieve 3 Å and 50 mg pyridinium dichromate. After 4 h at 7 °C the reaction mixture was washed two times with 2 ml water and 2 ml diluted hydrochloric acid. The organic phase was dried over sodium sulphate and chromatographed on silica gel with *n*-hexane. From an enriched fraction 1 mg of **5**, identical to the natural product, was isolated by preparative GC using a heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin column.

3.15. Hydrogenation of (−)-myli-4(15)-en-3-one (*5*)

To a solution of 100 μg (−)-myli-4(15)-en-3-one (**5**) in 500 μl *n*-hexane 50 μg Pd/C (10%) was added and H_2 bubbled through the solution After 4 h the solution was filtered to give (−)-dihydromylione A (**4**) identical to the natural product isolated from *M. taylorii*.

3.16. (−)-(6R,7S)-α-Taylorione (*7*)

4-[2,2-Dimethyl-3-(5-methylcyclopenta-1,4-dien-1-yl)-cyclopropyl]-butan- 2-one. Colorless oil; sense of optical rotation (benzene): (−); $RI_{CPSil\text{-}5}$ 1586; ^1H NMR (500.1 MHz, C_6D_6) $\delta = 0.70$ (1H, *dt*, $J = 6.3$ Hz, $J = 8.5$ Hz, 7-H), 0.95 (3H, *s*, 12-H_{Si}), 1.09 (3H, *s*, 13-H_{Re}), 1.27 (1H, *dd*, $J = 8.7$ Hz, $J = 1.9$ Hz, 6-H), 1.61 (1H, *m*, 8-H) 1.67 (3H, *s*, 14-H), 1.88 (1H, *m*, 8-H′), 1.95 (3H, *d*, $J = 1.0$ Hz, 15-H), 2.12 (2H, *m*, 9-H) 2.76 (2H, *t*, $J = 1.7$ Hz, 2-H), 6.01 (1H, *s*,*br*, 3-H), 6.04 (1H, *s*,*br*, 1-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 14.3$ (*q*, 15-C), 15.8 (*q*, 12-$C_{(Si)}$), 19.4 (*s*, 11-C), 20.7 (*t*, 8-C), 26.3 (*d*, 6-C), 28.7 (*d*, 7-C), 29.2 (*q*, 13-$C_{(Re)}$), 29.4 (*q*, 14-C), 40.0 (*t*, 2-C) 44.0 (*t*, 9-C), 127.3 (*d*, 1-C), 127.7 (*d*, 3-C), 136.6 (*s*, 4-C), 144.5 (*s*, 5-C), 206.1 (*s*, 10-C); MS (EI, 70 eV) *m*/*z* (rel. int.) : 218 (19) $[M]^+$, 203 (5), 185 (9), 175 (23), 160 (34), 147 (89), 145 (87), 131 (27), 119 (63), 105 (66), 91 (70), 77 (33), 65 (16), 55 (29), 43 (100).

3.17. Rearrangement of (−)-taylorione (*6*)

A solution of 3 mg (−)-**6** (isolated from *M. taylorii*) in 1 ml *n*-hexane was treated with 0.5 mg Amberlyst® 15. After 5 min the solution was filtered and submitted to GC-MS. Approx. 1 mg (−)-**7**, 1 mg (−)-**25** and 0.5 mg (−)-**26**, identical to the natural products, were isolated by preparative GC using a heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin column.

3.18. (−)-(7S)-(E)-Taylopyran (*25*)

2,2,6-Trimethyl-3-[(*E*)(2-methylcyclopenta-2-en-1-ylidene)methyl]-3,4-dihydro-2*H*-pyran. Colorless oil; sense of optical rotation (benzene): (−); $RI_{CPSil\text{-}5}$ 1536; ^1H NMR (500.1 MHz, C_6D_6) $\delta = 1.23$ (3H, *s*, 12-H_{Re}), 1.34 (3H, *s*, 13-H_{Si}), 1.68 (3H, *d*, $J = 1.3$ Hz, 15-H), 1.81 (3H, *s*,*br*, 14-H), 1.91 (1H, *ddt*, $^2J = 17.0$ Hz, $J = 9.1$ Hz, $J = 2.2$ Hz, 8-H_{Re}), 2.11 (1H, *d*,*br*, $^2J = 16.7$ Hz, 8-H_{Si}), 2.21 (2H, *m*, 2-H), 2.41 (2H, *m*, 1-H), 2.48 (1H, *dt*, $J = 6.0$ Hz, $J = 9.8$ Hz, 7-H), 4.50 (1H, *s*,*br*, 9-H), 5.12 (1H, *d*, $J = 10.1$ Hz, 6-H), 5.62 (1H, *s*, 3-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 13.1$ (*q*, 15-C), 21.0 (*q*, 14-C),

21.3 (*q*, 12-$C_{(Re)}$), 26.5 (*t*, 8-C), 27.9 (*t*, 1-C), 28.0 (*q*, 13-$C_{(Si)}$), 30.4 (*t*, 2-C), 42.7 (*d*, 7-C), 76.8 (*s*, 11-C), 93.9 (*d*, 9-C), 118.2 (*d*, 6-C), 133.9 (*d*, 3-C), 140.6 (*s*, 4-C), 148.8 (*s*, 5-C), 149.2 (*s*, 10-C); MS (EI, 70 eV) *m/z* (rel. int.) : 218 (24) $[M]^+$, 175 (10), 160 (5), 148 (100), 133 (40), 120 (16), 105 (33), 91 (30), 77 (19), 69 (14), 53 (11), 43 (38); HRMS $m/z = 218.1681$ $[M]^+$ (calc. for $C_{15}H_{22}O$: 218.1671).

3.19. (−)-(6S,7S,10R)-Taylocyclane (**26**)

1,3,3-Trimethyl-7-(5-methylcyclopenta-1,4-dien-1-yl)-2-oxabicyclo[2.2. 1]heptane. Colorless oil; sense of optical rotation (benzene): (−); $RI_{CPSil-5}$ 1477; ^1H NMR (500.1 MHz, C_6D_6) $\delta = 1.24$ (3H, *s*, 12-H_{Si}), 1.25 (3H, *s*, 13-H_{Re}), 1.47 (3H, *s*, 14-H), 1.52 - 1.59 (1H, *m*, 8-H_{Re}), 1.61–1.67 (1H, *m*, 9-H_{Re}), 1.67–1.73 (1H, *m*, 8-H_{Si}), 1.76–1.83 (1H, *m*, 9-H_{Si}), 1.91 (4H, *s*, 15-H, *m*, 7-H), 2.72 (2H, *s*,*br*, 2-H), 3.00 (1H, *s*,*br*, 6-H), 5.89 (1H, *s*,*br*, 1-H), 6.00 (1H, *s*, 3-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 14.6$ (*q*, 15-C), 19.0 (*q*, 14-C), 23.2 (*t*, 8-C), 26.3 (*q*, 12-$C_{(Si)}$), 29.7 (*q*, 13-$C_{(Re)}$), 34.2 (*t*, 9-C), 39.9, (*t*, 2-C), 51.2 (*d*, 7-C), 52.4 (*d*, 6-C), 78.0 (*s*, 11-C), 86.5 (*s*, 10-C), 127.0 (*d*, 1-C), 128.1 (*d*, 3-C), 143.7 (*s*, 4-C), 144.3 (*s*, 5-C); MS (EI, 70 eV) *m/z* (rel. int.) : 218 (34) $[M]^+$, 203 (6), 185 (11), 175 (28), 160 (48), 147 (100), 145 (179), 131 (22), 119 (44), 105 (43), 91 (43), 77 (20), 65 (10), 55 (16), 43 (56); HRMS $m/z = 218.1680$ $[M]^+$ (calc. for $C_{15}H_{22}O$: 218.1671).

3.20. (5S*,7S*)-Taylofuran (**27**)

4-(2,2,6-Trimethyl-1-oxaspiro[4.4]non-6-en-3-yl)-butan-2-one. Colorless oil; sense of optical rotation: (*n.d.*); $RI_{CPSil-5}$ 1634; ^1H NMR (500.1 MHz, C_6D_6) $\delta = 0.98$ (3H, *s*, 12-H_{Si}), 1.27 (3H, *s*, 13-H_{Re}), 1.30 (1H, *m*, 8-H), 1.43 (1H, *d*, $J = 3.8$ Hz, 6-H), 1.45 (1H, *s*, 6-H′), 1.52 (1H, *m*, 8-H′), 1.68 (3H, *s*, 14-H), 1.72 (3H, *d*, $J = 1.9$ Hz, 15-H), 1.76 (1H, *m*, 7-H), 1.80–1.91 (3H, *m*, 1-H, 9-H, 9-H′), 2.00–2.09 (2H, *m*, 1-H′, 2-H), 2.22 (1H, *m*, 2-H′), 5.40 (1H, *s*,*br*, 3-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 12.0$ (*q*, 15-C), 24.0 (*t*, 8-C), 24.3 (*q*, 12-$C_{(Si)}$), 29.0 (*t*, 2-C), 29.4 (*q*, 14-C), 29.9 (*q*, 13-$C_{(Re)}$), 39.7 (*t*, 6-C), 41.0 (*t*, 1-C), 42.8 (*t*, 9-C), 48.7 (*d*, 7-C), 81.6 (*s*, 11-C), 92.9 (*s*, 5-C), 126.6 (*d*, 3-C), 143.4 (*s*, 4-C), 205.7 (*s*, 10-C); MS (EI, 70 eV) *m/z* (rel. int.): 236 (15) $[M]^+$, 221 (4), 203 (6), 178 (63), 165 (9), 145 (15), 140 (18), 120 (74), 105 (33), 97 (67), 96 (72), 93 (51), 82 (69), 67 (45), 55 (36), 43 (100); HRMS $m/z = 236.1786$ $[M]^+$ (calc. for $C_{15}H_{24}O_2$: 236.1776).

3.21. (1R*,4S*,5R*,6S*,7R*,9R*)-Taynudol (**28**)

2,8-Dimethyl-5-methylene-2a,3,4,5,5a,6,7,8,8a,8b-decahydro-cyclobuta[*e*]azulen-4-ol. Colorless oil; sense of optical rotation: (*n.d.*); $RI_{CPSil-5}$ 1707; ^1H NMR (500.1 MHz, C_6D_6) $\delta = 0.93$ (3H, *d*, $J = 7.3$ Hz, 15-H), 1.31 (1H, *m*, 3-H_{Si}), 1.49 (3H, *d*, $J = 1.3$ Hz, 13-H), 1.53–1.64 (3H, *m*, 2-H_{Si}, 3-H_{Re}, 8-H_{Re}), 1.78 (1H, *m*, 2-H_{Re}), 2.03 (1H, *ddd*, $J = 13.1$ Hz, $J = 7.1$ Hz, $J = 3.2$ Hz, 8-H_{Si}), 2.11 (1H, *m*, 4-H), 2.16 (1H, *m*, 5-H), 2.48 (1H, *d.br*, $J = 13.9$ Hz, 7-H), 2.55 (1H, *d*,*br*, $J = 12.3$ Hz, 6-H), 3.03 (1H, *m*, 1-H), 4.03 (1H, *dd*, $J = 7.3$, $J = 9.5$ Hz, 9-H), 4.81 (1H, *s.br*, 14-H_E), 4.83 (1H, *s*,*br*, 14-H_Z), 5.76 (1H, *s*,*br*, 12-H); ^{13}C NMR (100.6 MHz, C_6D_6) $\delta = 14.3$ (*q*, 13-C), 17.2 (*q*, 15-C), 28.3 (*t*, 2-C), 32.7 (*t*, 8-C), 33.6 (*t*, 3-C), 38.2 (*d*, 4-C), 41.2 (*d*, 1-C), 41.6 (*d*, 6-C), 44.1 (*d*, 7-C), 45.3 (*q*, 5-C), 77.2 (*d*, 9-C), 111.4 (*t*, 14-C), 132.3 (*d*, 12-C), 147.6 (*s*, 11-C), 153.7 (*s*, 10-C); MS (EI, 70 eV) *m/z* (rel. int.): 218 (4) $[M]^+$, 203 (10), 200 (23), 185 (44), 171 (12), 157 (34), 143 (70), 129 (50), 119 (46), 105 (75), 91 (100), 77 (62), 67 (31), 55 (38), 41 (51); HRMS $m/z = 218.1683$ $[M]^+$ (calc. for $C_{15}H_{22}O$: 218.1671).

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