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Silvaglins and related 2,3-secodammarane derivatives – unusual types of triterpenes from *Aglaia silvestris*

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ABSTRACT

Lipophilic crude extracts of leaves, stem and root bark of six different provenances of *Aglaia silvestris* were compared to determine species-specific chemical trends as well as infraspecific variability. 3,4-Secodammarane triterpenes formed the basic chemical equipment accompanied by the 2,3-seco derivative aglasilvinic acid, probably representing the precursor of the silvaglin A and isosilvaglin A characterised by a five membered ring A. In addition, the pregnane steroid pregnacetal was isolated and identified together with the known sesquiterpenes α-muurolene and viridiflorol, and the bisamide pyramidatin. Depending on the collection site all major triterpenes showed two different stereochemical trends either towards 20*R* or 20*S* configuration, giving rise to isolation and identification of the two isomers methylisofoveolate B (20*S*,24*R*) and methylfoveolate B (20*R*,24*S*) as well as the known derivatives shoreic acid (20*S*,24*R*), isoeichlerianic acid (20*R*,24*S*), and methylisoeichleriate (20*R*,24*S*). The structures were elucidated by 2D-NMR experiments and silvaglin A additionally by X-ray diffraction. The structural diversity and distribution of triterpenoids within the genus *Aglaia* is highlighted with respect to chemotaxonomic implications.

1. Introduction

The chemotaxonomic significance of triterpenoid accumulation in Meliaceae has recently been discussed, indicating the wide distribution of dammarane and 3,4-secodammarane derivatives in *Aglaia* species (de Campos Braga et al., 2006). In addition, various derivatives of cycloartanes (Inada et al., 1997, 2001; Mohamad et al., 1997; Weber et al., 2000; Joycharat et al., 2008a), tirucallanes (Benosman et al., 1995; Puripattanavong et al., 2000), apotirucallanes (Mohamad et al., 1999a), glabretals (Mulholland and Monkhe, 1993; Su et al., 2006), baccharanes (Hwang et al., 2004a,b), and lupanes (Joycharat et al., 2008a) were also reported for the genus. Recently we established a new series of stereoisomeric 3,4-secodammaranes in *A. silvestris* (M. Roemer) Merrill, where the tetrahydrofuran (20,24-epoxy) ring linked to the D ring was characterised by the configuration 20*R*. Careful ^{13}C NMR analyses allowed the conclusion that foveolin B, previously described as 20*S*,24*R* (Roux et al., 1998), actually also belongs to the new 20*R*,24*S* series (Seger et al., 2008). In the course of clarifying the stereochemistry of the other triterpenes detected in *A. silvestris*, we now found the same configuration in other derivatives isolated from leaves, stem and root bark. However, a comparison of various geographical provenances, collected in south Thailand, exhibited the existence of two different chemo-types characterised either by 20*S* or 20*R* configuration. In this context two hitherto unknown triterpenes were also detected and isolated, representing an unusual type of derivatives with a five-membered A ring (**1**, **7**). In addition, a new 2,3-secodammarane derivative was identified, characterised by an acetal group at C2 (**8**). The detection of a new pregnane steroid with an acetal-group at C3 (**9**) was of some chemotaxonomic interest, since various pregnanes were already reported for different *Aglaia* species (Inada et al., 1997; Mohamad et al., 1999b; Qiu et al., 2001; Joycharat et al., 2008a). Apart from triterpenoids, the lipophilic extracts of all *A. silvestris* provenances were characterised by the two known sesquiterpenes viridiflorol (**10**) and α-muurolene (**11**). In the leaf extracts of four different collections the known bisamide pyramidatin was also detected. The present paper describes the isolation and identification of six new triterpenoids from which the structure of the novel silvaglin A (**1**) with a five-membered ring

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A was additionally confirmed by X-ray crystallographic analysis. The chemosystematic impact of different triterpene patterns within the genus *Aglaia* is discussed.

2. Results and discussion

In the present investigation $CHCl_3$ fractions of methanolic crude extracts of 6 different provenances of *A. silvestris*, collected in south and southeast Thailand, were analysed. The individual triterpene patterns of leaves, stem and root bark, were compared by TLC sprayed with anisaldehyde/sulfuric acid. All main components were isolated by preparative MPLC and TLC and their structures elucidated by 2D-NMR experiments. From the root bark of *A. silvestris* (HG 973), collected near Trat in southeast Thailand, a crystalline precipitate was obtained from a column fraction eluted with 40% EtOAc in hexane. First inspection of the ^1H and ^{13}C NMR data of compound **1** showed the typical resonances of dammarane triterpenes with a tetrahydrofuran (20,24-epoxy) substituent linked to the D ring. The ^{13}C NMR data of this epoxy ring, especially the indicative resonances of C21, C22, and C24 were identical with those of shoreic acid and the configurations could therefore be assigned unambiguously as 20*S*,24*R* (Seger et al., 2008). However, an additional aldehyde function was indicated in the ^1H NMR spectrum by a doublet at $\delta = 9.63$ ppm ($J = 4.0$ Hz). It coupled with another doublet at 2.89 ppm ($J = 4.0$ Hz). In the ^{13}C NMR spectrum the aldehydic carbon atom showed a characteristic signal for a CH doublet at 201.0 ppm. Comparison of the ^{13}C NMR data of compound **1** with other dammaranes (Tori et al., 1988) and secodammaranes (Seger et al., 2008) showed that major changes had occurred in the A ring. The resonances of the remaining ring systems B, C, D and the 20,24-epoxy side group were almost identical with other relevant dammaranes. HMBC allowed the identification of the methyl groups and the adjacent carbon atoms. Of special interest were the long range coupling cross peaks 19 → 10, 1, 5, 9; 28 → 4, 3, 5, 29; and 29 → 4, 3, 5, 28. Using these cross peaks, C1 was assigned to the carbon resonance at 75.6 ppm correlating to the ^1H NMR doublet at 2.89 ppm (HMQC), which in turn was linked to the formyl group (COSY). The above mentioned HMBC cross peaks confirmed the expected direct link of C3 (carbonyl) to the quaternary C4 $(CH_3)_2$. The only possible explanation of these data was the assumption of a ring closure C1–C3 to complete the A ring. The arguments outlined above resulted in a 5-membered A-ring with a formyl substituent attached to C1. In the numbering scheme of triterpenes the formyl group originated from the C2 methylene group after 2,3 ring opening followed by a 1,3 ring closure. Strong NOESY cross peaks between 1H and the α-positioned 5H and 9H allowed the conclusion that the aldehyde function was β-orientated. This was additionally confirmed by a strong cross peak between the aldehyde proton and the 19-methyl group. The new compound **1** with its rather unusual A ring contraction and a formyl group at position 1 (1H-α) was named silvaglin A. The isolated sample contained also a small amount of the isomeric 1H-β compound (**1a**, silvaglin B). The content was about 2.5%, after one month in $CDCl_3$ at 5 °C it increased to ca. 4%. Characteristic signals of **1a** were the aldehyde proton at 9.74 ppm ($J = 2.4$ Hz) and the vicinal 1H at 3.22 ppm ($J = 2.4$ Hz). Isomerisation of 1,3-dicarbonyl compounds is not unlikely due to the acidic character of the proton between the carbonyl groups. However, after crystallisation from ethanol pure crystals of silvaglin A (**1**) were obtained which were well suited for X-ray structure analysis.

The result of the X-ray structure determination is shown in Fig. 1 and technical details including bond lengths are given in the experimental Section (4.10). The X-ray structure confirmed the conclusions derived from the NMR experiments showing that all rings of the terpene moiety were *trans*-fused, and proved that C1 has an aldehyde function in β-orientation (Fig. 1). The two six-membered rings exhibited approximate chair-conformations. The three five-membered rings adopted envelope conformations with corresponding envelopes at C10, C13, and C22, respectively. All bond lengths were normal. Interesting bond and torsion angles (deg.) were: C1–C2–O1 126.9(3), C3–C1–C2–O1 43.6(4), C1–C3–C4 109.4(2), C1–C3–O2 125.9(2), C4–C3–O2 124.7(2), C13–C17–C20–O3 172.4(1), and O3–C24–C25–O4 178.1(1). Viewed along the *a*-axis of the unit cell the molecules of silvaglin A (**1**) adopted a herring-bone pattern in the solid state. The OH group of O4 formed an intermolecular hydrogen bond to the furan-oxygen O3 of a neighbouring molecule, O4–O3 = 2.972(2) Å. The carbonyl oxygen O2 was acceptor of two intermolecular C–H–O interactions with C1–O2 = 3.227(2) Å and C9–O2 = 3.336(2) Å.

Column fractions eluted with 50% and 70% EtOAc in hexane yielded the compounds **2** and **3**, respectively. Whereas the NMR-data of **3** were shown to be identical with those of the well-known 3,4-secodammarane shoreic acid, compound **2** represented a new derivative. ^1H and ^{13}C NMR data showed that compound **2** was closely related to foveolin A and B. In the ^1H NMR spectrum the triplet at 3.72 ppm was characteristic for 24H in the 20,24-epoxide side chain. In the ^{13}C NMR spectrum four characteristic low field resonances, due to neighbouring oxygen atoms, were indicative for foveolins: 86.3 (*s*, C20), 83.3 (*d*, C24), 75.8 (*s*, C4), and 71.4 ppm (*s*, C25) (Roux et al., 1998). Additional characteristic signals at 175.6 (*s*, C3) and 51.6 ppm (ester OMe), and a corresponding proton resonance singlet of 3H at 3.66 ppm proved that compound **2** was a methyl ester of the foveolate type. The epoxide configuration 20*S*,24*R* of compound **2** followed from the characteristic ^{13}C resonances of C21 (23.4 ppm), C22 (35.9 ppm), and C24 (83.3 ppm) (Seger et al., 2008). An identical structure of **2** has already been published and named dymalol (Govindachari et al., 1994). However, the stereochemistry of dymalol was described incorrectly and later corrected to be 20*S*,24*S* by esterification of foveolin A (Roux et al., 1998). The corresponding acid to compound **2** has

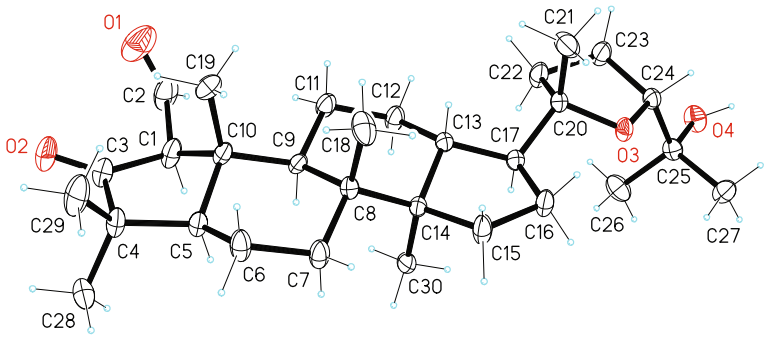

Fig. 1. Thermal ellipsoid representation of silvaglin A (**1**) in solid state showing the adopted chemical atom numbering.

not been described yet. Foveolin A is characterised by 20*S*,24*S* configuration and the isomeric foveolin B was erroneously described as 20*S*,24*R* (Roux et al., 1998), but recently corrected to be 20*R*,24*S* (Seger et al., 2008). The newly described foveolin ester with 20*S*,24*R* configuration was designated as methylisofoveolate B (**2**). The ^{13}C NMR data, listed in Table 1, were assigned using 2D techniques (HH-COSY, NOESY, HMQC, HMBC).

According to our previous paper the root bark of another provenance of *A. silvestris* (HG 719), collected in Khao Chong, near Trang in south Thailand, afforded the recently described isoeichlerianic acid (**4**) and its methyl ester **5**. Both belong to the newly established 20*R*,24*S* epoxide series of dammaranes (Seger et al., 2008). More detailed chromatographic separations led to the isolation of a series of further new triterpenes. Compound **6** showed ^{1}H and ^{13}C NMR spectra which were almost identical with those of methylisofoveolate B (**2**). The only significant exceptions were the ^{13}C NMR resonances of C21, C22, and C24. The shift values of these carbon atoms were 21.8, 37.4, and 84.4 ppm, respectively, clearly indicating 20*R*,24*S* configuration of the epoxide ring (Seger et al., 2008). This corresponded to the corrected stereochemistry of foveolin B and therefore compound **6** was named methylfoveolate B.

The ^{13}C NMR spectrum of compound **7** was almost identical with that of silvaglin A (**1**). Again only the chemical shifts for C21, C22, and C24 were slightly but significantly different with values at 21.6, 37.5, and 84.4 ppm, respectively (Table 1). From this it follows that the stereochemistry of the epoxide ring was 20*R*,24*S* in comparison to **6**. Strong NOESY cross peaks 1H ↔ 5-Hα and 2H (formyl) ↔ 19H_3 confirmed the β-position of the aldehyde function (1Hα). The compound was designated as isosilvaglin A. Even after careful TLC separation the sample contained two further minor constituents of ca. 15% each. One was the 1H-β isomer of isosilvaglin A which was characterised by an aldehyde proton at 9.74 ppm (J = 2.3 Hz) and the vicinal 1H at 3.23 ppm (J = 2.3 Hz) (compare discussion of silvaglin B). In analogy to silvaglin B this compound was named isosilvaglin B (**7a**). The second contamination was most likely a product with a double bond in the 5-ring (**7b**). The olefinic proton 3H showed resonance at 4.79 ppm (singlet). The aldehyde proton 2H was also a singlet at 9.89 ppm. A clear NOESY cross peak between the singlets 2H ↔ 3H supported the structure. Consequently **7b** was designated as desoxysilvaglin and may be regarded as reduction product of the carbonyl function at C3 to 3-OH, followed by loss of H_2O (Fig. 2).

Table 1
^{13}C NMR data of 20,24-epoxydammaranes **1**, **2**, and **6**–**8** and pregnane **9** (in $CDCl_3$)

No.	1	2	6	7	8	9
1	75.6 *d*	34.6 *t*	34.6 *t*	75.6 *d*	41.0 *t*	34.7 *t*
2	201.0 *d*	28.9 *t*	28.9 *t*	200.9 *d*	101.4 *d*	28.3 *t*
3	217.4 *s*	175.6 *s*	175.7 *s*	217.5 *s*	183.1 *s*	100.3 *s*
4	46.2 *s*	75.8 s	75.8 *s*	46.2 *s*	46.3 *s*	35.5 *t*
5	59.4 *d*	51.9 *d*	51.6 *d*	59.4 *d*	49.3 *d*	42.3 *d*
6	17.2 *t*	22.6 *t*	22.6 *t*	17.2 *t*	20.5 *t*	28.2 *t*
7	34.5 *t*	34.6 *t*	34.6 *t*	34.5 *t*	35.0 *t*	32.0 *t*
8	41.6 *s*	40.0 *s*	40.0 *s*	41.6 *s*	40.1 *s*	34.2 *d*
9	49.6 *d*	42.4 *d*	42.3 *d*	50.1 *d*	43.3 *d*	53.4 *d*
10	47.1 *s*	41.2 *s*	41.2 *s*	47.1 *s*	41.9 *s*	35.8 *s*
11	24.9 *t*	21.3 *t*	21.2 *t*	24.8 *t*	22.7 *t*	20.0 *t*
12	26.8 *t*	27.4 *t*	27.1 *t*	26.5 *t*	26.8 *t*	29.9 *t*
13	42.7 *d*	43.1 *d*	43.0 *d*	42.6 *d*	42.8 *d*	44.1 *s*
14	50.1 *s*	50.4 *s*	50.3 *s*	50.0 *s*	50.3 *s*	45.4 *d*
15	31.5 *t*	31.4 *t*	31.2 *t*	31.2 *t*	31.1 *t*	37.0 *t*
16	25.5 *t*	25.7 *t*	25.8 t	25.6 *t*	25.9 *t*	222.3 *s*
17	49.3 *d*	49.5 *d*	50.0 *d*	49.2 *d*	49.7 *d*	81.0 *s*
18	15.8 *q*	15.3 *q*	15.3 *q*	15.9 q	15.6 *q*	13.6 *q*
19	15.6 *q*	20.5 *q*	20.5 *q*	15.5 *q*	20.6 *q*	11.6 *q*
20	86.2 *s*	86.3 *s*	86.4 *s*	86.2 *s*	86.5 *s*	68.0 *d*
21	23.5 *q*	23.4 *q*	21.8 *q*	21.6 *q*	21.9 *q*	16.0 *q*
22	35.8 *t*	35.9 *t*	37.4 *t*	37.5 *t*	37.5 *t*	
23	26.1 *t*	26.1 *t*	25.8 *t*	25.7 *t*	25.9 *t*	
24	83.3 *d*	83.3 *d*	84.4 *d*	84.4 *d*	84.4 *d*	
25	71.4 *s*	71.4 *s*	71.1 *s*	71.1 *s*	71.1 *s*	
26	27.4 *q*	27.4 *q*	27.7 *q*	27.6 *q*	27.8 *q*	
27	24.3 *q*	24.3 *q*	24.3 *q*	24.3 *q*	24.3 *q*	
28	27.9 *q*	34.1 *q*	34.1 *q*	27.9 *q*	28.3 *q*	
29	21.0 *q*	27.4 *q*	27.4 *q*	21.0 *q*	23.3 *q*	
30	16.5 *q*	16.2 *q*	15.9 *q*	16.3 *q*	15.9 *q*	
OMe (ester or acetal)		51.6 *q*	51.9 *q*		54.2 *q*	47.47 *q*
					49.9 *q*	47.51 *q*

Compound **8** showed again NMR data typical for the dammarane series with a 20,24-epoxide ring system characterised by a 20*R*,24*S* configuration, as shown for methylfoveolate B (**6**) and isosilvaglin A (**7**) (compare the diagnostic ^{13}C NMR shifts for C21, C22, and C24 in Table 1). The ^{13}C chemical shifts of rings C and D including the side chain of ring D were almost identical with those of compounds **6** and **7**, however ring A and partially also ring B differed dramatically. The ^{13}C resonance at 101.4 ppm (with a corresponding ^{1}H resonance at 4.68 ppm), together with two methoxy groups at 54.2 and 49.9 ppm (^{1}H 3.33 and 3.22 ppm) suggested an acetal function. In addition, a quaternary ^{13}C resonance at 183.1 ppm indicated a carboxylic acid as a further functional group. The molecular formula $C_{32}H_{56}O_6$ deduced from the peak $[M + Na]^+$ at m/z 559 in the ESI mass spectrum was in agreement with these functions in addition to the classical dammarane structure with an epoxide and a tertiary OH in the side chain. Details for the structure of ring A were obtained by means of 2D NMR (HH-COSY, NOESY, HMBC, HMQC). The long range cross peaks of methyl-19 allowed to identify C10, 1, 5, and 9. The geminal methyl groups 28 and 29 showed long range contacts to C4, 3, and 5 (and to each other). HMQC allowed to assign the diastereomeric protons $1H_2$ at 1.86 ppm and 1.65 ppm. In the ^{1}H NMR spectrum the acetalic 2H showed H,H-COSY cross peaks to both protons $1H_2$, a strong one to 1.86 ppm and a weak one to 1.65 ppm. In $CDCl_3$ the acetalic 2H resonance appeared as a broad doublet at 4.68 ppm with J = 7.0 Hz, in acetone-d_6 a clear *dd* at 4.74 ppm with J = 6.6 and 2.3 Hz was obtained. The side chain –CH_2–$CH(OCH_3)_2$ attached to C10 was confirmed by strong long range cross peaks from both acetalic methoxy groups and from the 1-H_2 protons to the acetalic C2 between. The identification of C10 and C1 followed from long range contacts of methyl-19, proving the connectivities 19–10–1–2. The α-position of the acetalic side chain could be derived from NOESY cross peaks of the acetalic 2H with the α-orientated protons 5H at 2.01 ppm and 9H at 1.70 ppm (5H and 9H were identified by HMQC). A strong NOESY cross peak between 2H and the acetalic OMe group at 3.33 ppm and a rather weak one to OMe at 3.22 ppm was in agreement with the rather constricted rotation about the C1–C2 bond which followed also from the rather different coupling constants $J_{1a,2}$ and $J_{1b,2}$ resulting in a broad doublet for the 2H resonance in $CDCl_3$ (see above). A further side chain at C5 was β-orientated (5H-α) and was formed by the remaining carbon atoms numbers 4 and 3 of the dammarane A-ring. The side chain –$C(CH_3)_2$–COOH followed from the long range contacts of the methyl groups 28 and 29 establishing the connectivities 28, 29–4–3. Since both side chains contained terminal functions like the aldehyde derived $CH(OMe)_2$ group and carboxylic acid, compound **8** was necessarily a new 2,3-seco derivative, named aglasilvinic acid (**8**). With respect to the widespread occurrence of 3,4-seco-dammaranes in *Aglaia* this structure was rather unusual and turned out to be of special biosynthetic interest regarding the formation of the silvaglines. In this case a cyclisation step between C1 and C3 could be expected leading to the 1-formyl five-membered rings (**1**, **7**) (Fig. 2).

Compound **9** contained also an acetalic function derived from a ketone which was indicated by a quaternary acetalic ^{13}C resonance at 100.3 ppm together with two OMe signals at 47.47 and

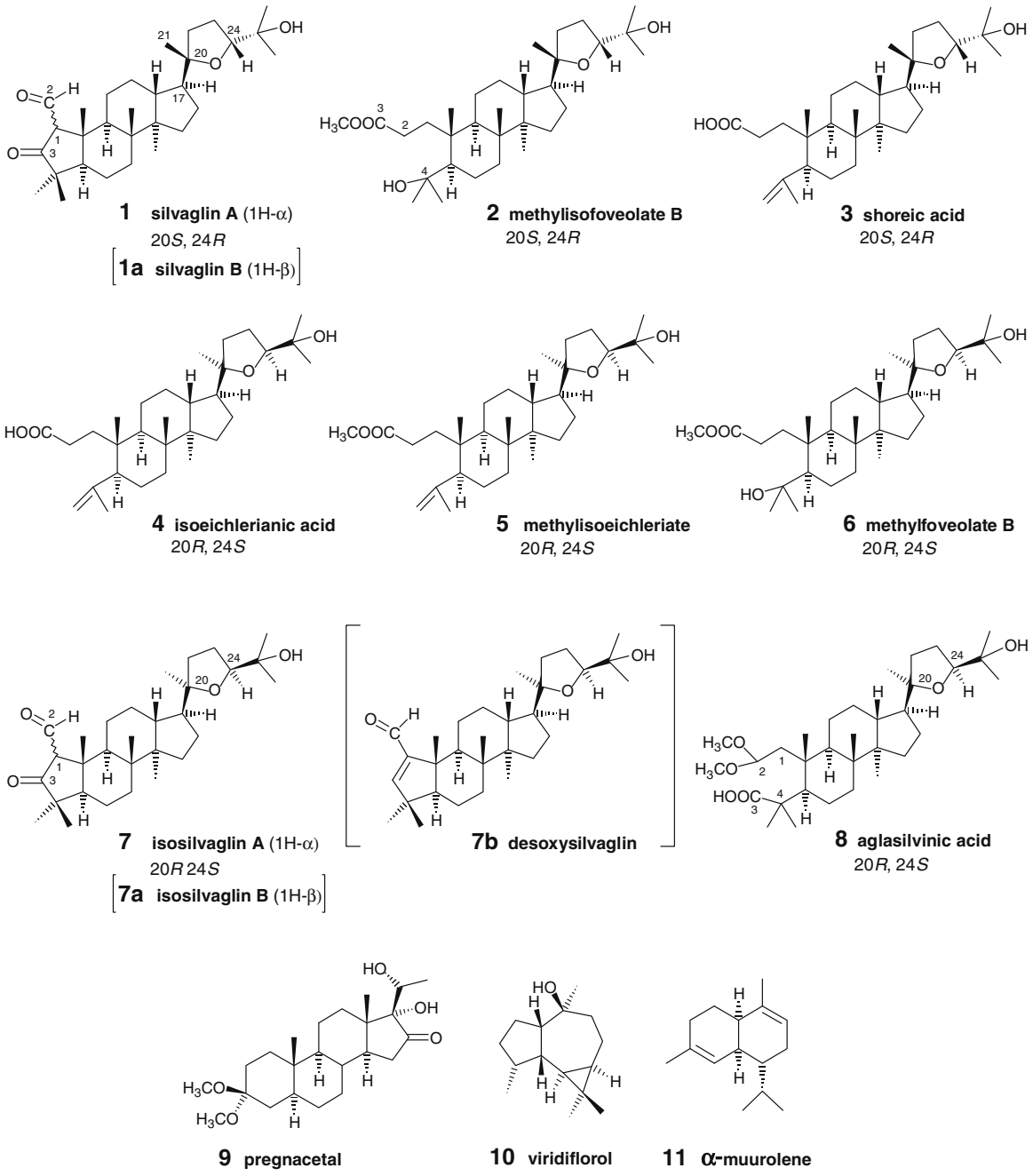

Fig. 2. Terpenoids of *A. silvestris*. Compounds in brackets represent minor derivatives detected as mixtures with silvaglin A (**1**) and isosilvaglin A (**7**), respectively.

47.51 ppm with corresponding ^{1}H OMe resonances at 3.19 and 3.14 ppm. ^{13}C-Database search (Robien, 1998; Seger et al., 1997) revealed that the compound was a C3 acetalic derivative of 17α,20*R*-dihydroxypregnan-3,16-dione (Luo et al., 2000). Only the resonances of the A-ring differed significantly from the corresponding reference data. The decision whether the 3CO or 16CO group had been transformed into dimethoxy was clear because the two carbonyl shifts of the 3,16-dione were rather different: C3 at 211.2 and C16 at 221.7 ppm (Luo et al., 2000). In our case a carbonyl resonance was found at 222.3 ppm, the other one was missing. Strong NOESY cross peaks between $3(OMe)_2 \leftrightarrow 2H_2$, $4H_2$ and a weak one to 5H confirmed the C3 position of the acetalic OMe groups. The pregnane derivative **9** (17α,20*R*-dihydroxy-3,3-dimethoxypregnan-16-one) was designated as pregnacetal. The sesquiterpenes **10** and **11** were already known. Viridiflorol (**10**) has been isolated from 'niaouli' essential oil from leaves of *Melaleuca viridiflora* (Faure et al., 1991) and α-muurolene (**11**) from marine organisms like the soft-coral *Heteroxenia fuscescens* (Kashman et al., 1978; erroneously named α-murrolene or α-mullolene) and the sponge *Acanthella cavernosa* (Hirota et al., 1996).

Stimulated by the stereochemical differences of triterpenes between HG 973 and HG 719, TLC-profiles of crude extracts of four further collections (HG 679, HG 832, HG 941, HG 1010) were compared to get more insight into the chemical variability within the species. Apart from HG 719, a common trend towards 20*R* configuration in all major derivatives was also observed in two collections from different habitats in Khao Chong (HG 679, HG 1010) and one from Ton Nga Chang, near Hat Yai (HG 832). By contrast, derivatives of the 20*S* series, already described for HG 973 (Seger et al., 2008), were found in a collection from Similan Islands (HG

941). Based on colour reactions and low Rf-values, the corresponding free acids of the esters **2** and **6** may also be expected in the crude extracts, but could not be isolated in the present investigation. The distribution of pregnacetal (**9**) was not determined for all collections because of the weak yellowish colour-reaction with anisaldehyde on TLC and overlapping with other compounds. The terpenoid pattern outlined above mainly accumulated in stem and root bark, but was also present in smaller quantities in the leaf extracts.

3. Concluding remarks

With respect to storage of crude extracts in methanolic solution, containing eventually traces of $CHCl_3$ from the preceding extraction, it cannot be excluded that the compounds **2**, **5**, **6**, **8**, and **9** might be products of artefactual methylation. However, compounds **1**, **3**, **4**, **7**, and **8** still contain unmethylated aldehyde or carboxylic acid functions. Because of the limited quantities of plant material available for comparative studies, a re-investigation with another solvent was beyond the scope of this investigation. Comparing the literature on *Aglaia* triterpenes, the formation of various derivatives suggested two major enzymatic activities acting independently on two different sites of the triterpenic molecule. As already pointed out in our previous publication, the enzymatic oxidation of the side-chain at C17 obviously takes place independently from different formations of the cyclic sterane skeleton (Joycharat et al., 2008a). A biosynthetic sequence for the formation of different heterocyclic systems of the side-chain was recently suggested for *A. oligophylla* Miq. by the co-occurrence of open-chained derivatives together with two types of cyclic products with tetrahydrofuran (20,24-epoxy) and tetrahydropyran (20,25-epoxy) rings (Joycharat et al., 2008b). Another type of tetrahydrofuran ring in the side-chain was reported for *A. argentea* Blume, where an 21,23-epoxy ring was formed in the leaves (Omobuwajo et al., 1996a; Mohamad et al., 1997), seeds (Omobuwajo et al., 1996b), and stem bark (Mohamad et al., 1999a), probably representing the precursor of the terminal furan ring typical for limonoids. A similar trend towards an 21,23-epoxy ring was also reported for the bark of *A. crassinervia* Kurz ex Hiern with an additional formation of a tetrahydropyran (21,24-epoxy) ring (Su et al., 2006). In contrast to the triterpenes of *A. argentea*, characterised by cycloartanes or apotirucallanes, those from *A. crassinervia* deviated by dammaranes and glabretals. Some species appeared to be uniformly characterised by a single structural type, like e.g. dammaranes in the present investigation or in *A. perviridis* Hiern, with two novel *abeo*-derivatives forming a six-membered acetal ring (Yang et al., 2008), whereas others show a combination of different types. Moreover, distinct structural types may be confined to different plant parts, as shown in *A. argentea* with many cycloartane derivatives in the leaves (Omobuwajo et al., 1996a), whereas apotirucallanes were isolated from the seeds and stem bark (Omobuwajo et al., 1996b). Generally, dammaranes and cycloartanes represented the most widespread triterpenes within the genus (Eck, 2004).

3,4-Seco-derivatives were shown to be widespread in *Aglaia*, mostly derived from dammaranes, but were also known from apotirucallanes (Omobuwajo et al., 1996b; Mohamad et al., 1999a) and baccharanes (Salim et al., 2007). Hence, the present discovery of the 2,3-seco-derivative aglasilvinic acid (**8**) was of special structural significance. Even more, as the characteristic compounds silvaglin A (**1**) and isosilvaglin A (**7**) with a five-membered ring A were most likely derived from such a precursor. Removal of methyl groups at C4 and C14 led to the formation of nortriterpenes (steroid triterpenes) and sterols (e.g. Rivero-Cruz et al., 2004). A dominant trend towards demethylation of a cycloartane precursor at C4 was reported for the leaves of Thai provenances of *A. elaeagnoidea* (A. Juss.) Benth. (Brader et al., 1998) and was also known from *A. roxburghiana* Miq. from India (Vishnoi et al., 1988; Balakrishna et al., 1990), a synonym of *A. elaeagnoidea* (Pannell, 1992). Of special chemotaxonomic significance was the discovery of limonoids of the gedunin type in *A. elaeagnoidea* from Indonesia (Fuzzati et al., 1996) and Australia (Hofer, 2002). Although representing a typical chemical character of the family Meliaceae, limonoids appeared to be only rarely produced in the genus *Aglaia*. With the formation of dammaranes and a different substitution pattern of flavaglines the two collections from Indonesia and Australia also clearly deviated from those originating from Thailand and India. A corresponding taxonomic segregation within this complex species has recently also been suggested by DNA sequencing (Muellner et al., 2009).

Shortening of the side chain resulted in the formation of pregnane and androstane-type steroids. Whereas the latter were only known so far from *A. rubiginosa* (Hiern) Pannell (Weber et al., 2000), pregnane steroids were already reported for *A. grandis* Korth. (Inada et al., 1997), *A. tomentosa* Teijsm. & Binn (Mohamad et al., 1999b), *A. lawii* (Wight) Saldanha ex Ramamoorthy (Qiu et al., 2001), and *A. forbesii* King (Joycharat et al., 2008a). The new pregnacetal (**9**), isolated from *A. silvestris*, shared the common carbonyl group at C16, but differed from the other derivatives by an acetal group at C3. Important for chemotaxonomic considerations was the general lack of flavagline accumulation in all provenances of *A. silvestris*, otherwise representing a characteristic chemical feature of the genus. In fact, this class of compounds was not described so far for any other plant family (Greger et al., 2001; Proksch et al., 2001). The previous report on flavaglines in *A. silvestris* (Hwang et al., 2004a) was later corrected in an erratum, where it was shown that they were actually isolated from *A. foveolata* C.M. Pannell (Hwang et al., 2004b). Even though no flavaglines were found in the present investigation, the presence of the genus-specific bisamide pyramidatin, detected in different quantities in four provenances of *A. silvestris*, supported the affiliation to *Aglaia*. The present comparison of different geographical provenances revealed a species-specific triterpene pattern, basically characterised by 3,4-secodammarane derivatives, but with an additional formation of 2,3-seco derivatives, most likely leading to the silvagline group with a five-membered ring A. Moreover, depending on the place of collection the triterpenes showed two different stereochemical trends either towards 20*S* or 20*R* configuration, suggesting different genetically fixed enzymatic activities.

4. Experimental

4.1. General

Mps: Kofler hot stage, uncorr. NMR: Bruker, DRX 400 WB ($CDCl_3$, ^1H δ 7.26, ^{13}C δ 77.0). MS: Finnigan MAT 900 S. IR: Perkin–Elmer 16PC FT-IR Spectrometer. Optical rotation: Perkin–Elmer Polarimeter 241.

4.2. Plant material

Leaves, stem and root bark of six different provenances of *A. silvestris* were collected separately in S- and SE-Thailand: (a) from Khao Chong waterfall, near Trang (HG 679, HG 719, HG 1010), (b) from Ton Nga Chang National Park, near Hat Yai (HG 832), (c) from Agro Forestry Station near Trat (HG 973), and (d) from Similan Islands, Phang Nga Province (HG 941). Voucher specimens were deposited at the Herbarium of the Faculty Center of Botany, University of Vienna, Austria, WU.

4.3. Extraction and isolation

Dried leaves, stem and root bark of six different collections of *A. silvestris* were ground separately and extracted twice with MeOH

at room temperature for 5 days, filtered, and concentrated. After addition of H_2O the aqueous residues were extracted with $CHCl_3$, evaporated to dryness, and dissolved in MeOH. This solution was stored at −20 °C and used for comparative TLC and further studies. For preparative isolation, lipophilic crude extracts were roughly separated by column chromatography (Merck Silica gel 60, 0.2–0.5 mm) with solvent mixtures of hexane, EtOAc and MeOH. Further separation was achieved by MPLC (400 × 40 mm column, Merck LiChroprep silica gel 60, 40–63 μm) with mixtures of MeOH in EtOAc and prep. TLC: silica gel 60 (Merck, F_{254} 0.5 mm).

From 28 g dried roots of *A. silvestris* (HG 719) a portion (1.5 g) of the $CHCl_3$ fraction (2.05 g) was roughly separated by CC eluted with increasing amounts of EtOAc (0–100%) in hexane. The fraction eluted with 10% EtOAc in hexane afforded 20 mg pure α-muurolene (**11**), while that with 30% EtOAc in hexane (250 mg) was further separated by MPLC (5% EtOAc in hexane) and prep. TLC (30% Et_2O in hexane, 3 times) to afford 15 mg viridiflorol (**10**) and 7 mg methylisoeichleriate (**5**). A further MPLC fraction (50% EtOAc in hexane) was separated by prep. TLC (50% Et_2O in hexane) leading to a mixture (10 mg) of isosilvaglin A (**7**) with traces of isosilvaglin B (**7a**) and desoxysilvaglin (**7b**). The CC fraction eluted with 40% EtOAc in hexane afforded 9 mg pregnacetal (**9**) and that with 50% EtOAc (200 mg) was further separated by repeated (cyclic) MPLC (30% EtOAc in hexane) to afford 8 mg aglasilvinic acid (**8**) and impure isoeichlerianic acid (**4**), which was purified by prep. TLC (3% MeOH in CH_2Cl_2) leading to 15 mg pure compound. A further cyclic MPLC fraction was separated by prep. TLC (30% EtOAc in CH_2Cl_2) to afford 9 mg methylfoveolate B (**6**).

The root extract of HG 973 (35 g) was analysed as described above. A portion (1.8 g) of the $CHCl_3$ fraction was roughly separated by CC. From the fraction eluted with 40% EtOAc in hexane 26 mg of a crystalline precipitate was obtained consisting mainly of silvaglin A (**1**) and small amounts (2.5%) of silvaglin B (**1a**). The fractions eluted with 50% and 70% EtOAc in hexane afforded 24 mg methylisofoveolate B (**2**) and 8 mg shoreic acid (**3**), respectively, after purification with prep. TLC (58% $CHCl_3$: 38% EtOAc: 2% MeOH: 2% Et_2O).

*4.4. Silvaglin A [20S,24R-epoxy-25-hydroxy-2-oxo-1(2 → 3)abeo-1α(H)-dammaran-3-one] (**1**)*

Colourless crystals, m.p. 175–178 °C; $[\alpha]_D^{20}$ = +22° (*c* = 0.7, $CHCl_3$). IR ν_{CCl4} cm^{-1} 3580 *w*, 2969 *s*, 2868 *s*, 2739 *w*, 1744 *s*, 1716 *m*, 1662 *m*, 1600 *w*, 1466 *m*, 1451 *m*, 1384 *s*, 1337 *w*, 1310 *w*, 1222 *w*, 1185 *w*, 1132 *w*, 1089 *m*, 991 *w*, 950 *w*. ^{1}H NMR ($CDCl_3$, methine resonances from 2D) δ/ppm = 9.63 (*d*, 1H, *J* = 4.0 Hz, 2-H), 3.72 (*t*, 1H, *J* = 7.3 Hz, 24-H), 2.89 (*d*, 1H, *J* = 4.0 Hz, 1-H), 1.86 (*m*, 1H, 9-H), 1.82 (*m*, 1H, 17-H), 1.56 (*m*, 1H, 13-H), 1.52 (*m*, 1H, 5-H), 1.20 (*s*, 3H, 26-Me), 1.19 (*s*, 3H, 19-Me), 1.12 (*s*, 3H, 21-Me), 1.11 (*s*, 3H, 27-Me), 1.07 (*s*, 3H, 29-Me), 1.06 (*s*, 3H, 28-Me), 0.99 (*s*, 3H, 18-Me), 0.92 (*s*, 3H, 30-Me). EIMS *m*/*z* = 472 (2%, M^+, $C_{30}H_{48}O_4$), 457 (7, M^+–Me), 413 (25), 395 (11), 371 (10), 165 (18), 143 (100), 85 (26).

*Silvaglin B [20S,24R-epoxy-25-hydroxy-2-oxo-1(2 → 3)abeo-1β(H)-dammaran-3-one] (**1a**).* ^{1}H NMR ($CDCl_3$) δ/ppm = 9.74 (*d*, 1H, *J* = 2.4 Hz, 2-H), 3.73 (*t*, 1H, *J* = 7.3 Hz, 24-H), 3.22 (*d*, 1H, *J* = 2.4 Hz, 1-H). ^{13}C NMR ($CDCl_3$) δ/ppm = 75.9 (*d*, C-1).

*4.5. Methylisofoveolate B [methyl 20S,24R-epoxy-4,25-dihydroxy-3,4-secodammaran-3-oate] (**2**)*

Amorphous powder $[\alpha]_D^{20}$ = +34° (*c* = 1.2, $CHCl_3$). IR ν_{CCl4} cm^{-1} 3579 *w*, 3505 *w*, 2965 *s*, 2871 *m*, 1740 *m*, 1604 *w*, 1465 *m*, 1456 *m*, 1384 *m*, 1376 *m*, 1310 *w*, 1260 *w*, 1180 *m*, 1124 *w*, 1082 *w*, 1055 *w*, 1022 *w*, 991 *w*, 951 *w*. ^{1}H NMR ($CDCl_3$, methine resonances from 2D) δ/ppm = 3.72 (*t*, 1H, *J* = 7.4 Hz, 24-H), 3.66 (*s*, 3H, COOMe), 2.48 (*m*, 1H, 1-Ha), 2.46 (*m*, 1H, 2-Ha), 2.18 (*m*, 1H, 2-Hb), 1.72 (*m*, 1H, 1-Hb), 1.81 (*m*, 1H, 17-H), 1.58 (*m*, 1H, 13-H), 1.52 (*m*, 1H, 9-H), 1.33 (*m*, 1H, 5-H), 1.28 (*s*, 3H, 28-Me), 1.24 (*s*, 3H, 29-Me), 1.20 (*s*, 3H, 26-Me), 1.13 (*s*, 3H, 21-Me), 1.11 (*s*, 3H, 27-Me), 1.00 (*s*, 3H, 19-Me), 0.97 (*s*, 3H, 18-Me), 0.86 (*s*, 3H, 30-Me). EIMS *m*/*z* = 488 (2%, M^+–18; $C_{31}H_{54}O_5$–H_2O), 430 (5), 143 (100), 125 (15), 85 (22), 59 (23).

*4.6. Methylfoveolate B [methyl 20R,24S-epoxy-4,25-dihydroxy-3,4-secodammaran-3-oate] (**6**)*

Amorphous powder $[\alpha]_D^{20}$ = +15° (*c* = 0.6, $CHCl_3$). IR ν_{CCl4} cm^{-1} 3572 *w*, 3503 *w*, 2964 *s*, 2872 *m*, 1738 *m*, 1578 *w*, 1562 *w*, 1458 *w*, 1377 *m*, 1305 *w*, 1168 *m*, 1120 *w*, 1084 *w*, 1053 *w*, 1022 *w*, 951 *w*. ^{1}H NMR ($CDCl_3$, methine resonances from 2D) δ/ppm = 3.75 (*t*, 1H, *J* = 7.3 Hz, 24-H), 3.67 (*s*, 3H, COOMe), 2.48 (*m*, 1H, 1-Ha), 2.45 (*m*, 1H, 2-Ha), 2.18 (*m*, 1H, 2-Hb), 1.72 (*m*, 1H, 1-Hb), 1.80 (*m*, 1H, 17-H), 1.58 (*m*, 1H, 13-H), 1.52 (*m*, 1H, 9-H), 1.34 (*m*, 1H, 5-H), 1.28 (*s*, 3H, 28-Me), 1.24 (*s*, 3H, 29-Me), 1.20 (*s*, 3H, 26-Me), 1.14 (*s*, 3H, 21-Me), 1.10 (*s*, 3H, 27-Me), 1.01 (*s*, 3H, 19-Me), 0.98 (*s*, 3H, 18-Me), 0.86 (*s*, 3H, 30-Me). EIMS *m*/*z* = 488 (2%, M^+–18; $C_{31}H_{54}O_5$–H_2O), 428 (4), 143 (100), 125 (18), 85 (20), 59 (25).

*4.7. Isosilvaglin A [20R,24S-epoxy-25-hydroxy-2-oxo-1(2 → 3)abeo-1α(H)-dammaran-3-one] (**7**)*

Colourless oil $[\alpha]_D^{20}$ = +47° (*c* = 0.5, $CHCl_3$). IR ν_{CCl4} cm^{-1} 3572 *w*, 2966 s, 2869 *m*, 2738 *w*, 1742 *m*, 1716 *w*, 1660 *w*, 1620 *m*, 1597 *m*, 1466 *m*, 1376 *s*, 1337 *w*, 1250 *w*, 1186 *w*, 1168 *w*, 1084 *m*, 1052 *w*, 990 *w*, 950 *w*. ^{1}H NMR ($CDCl_3$, methine resonances from 2D) δ/ppm = 9.63 (*d*, 1H, *J* = 3.9 Hz, 2-H), 3.74 (*t*, 1H, *J* = 7.2 Hz, 24-H), 2.89 (*d*, 1H, *J* = 3.9 Hz, 1-H), 1.80 (*m*, 1H, 9-H), 1.84 (*m*, 1H, 17-H), 1.68 (*m*, 1H, 13-H), 1.53 (*m*, 1H, 5-H), 1.20 (*s*, 3H, 26-Me), 1.19 (*s*, 3H, 19-Me), 1.12 (*s*, 3H, 21-Me), 1.10 (*s*, 3H, 27-Me), 1.07 (*s*, 3H, 29-Me), 1.06 (*s*, 3H, 28-Me), 0.99 (*s*, 3H, 18-Me), 0.92 (*s*, 3H, 30-Me). EIMS *m*/*z* = 472 (2%, M^+, $C_{30}H_{48}O_4$), 457 (6, M^+–Me), 413 (18), 395 (8), 371 (10), 165 (27), 143 (100), 125 (37), 85 (47).

*Isosilvaglin B [20R,24S-epoxy-25-hydroxy-2-oxo-1(2 → 3)abeo-1β(H)-dammaran-3-one] (**7a**).* ^{1}H NMR ($CDCl_3$) δ/ppm = 9.74 (*d*, 1H, *J* = 2.3 Hz, 2-H), 3.23 (*d*, 1H, *J* = 2.3 Hz, 1-H). ^{13}C NMR ($CDCl_3$) δ/ppm = 75.9 (*d*, C-1).

*Desoxysilvaglin B [20R,24S-epoxy-25-hydroxy-2-oxo-1(2 → 3)-abeo-1α(H)-dammar-1(3)-ene] (**7b**).* ^{1}H NMR ($CDCl_3$) δ/ppm = 9.89 (*s*, 1H, 2-H), 4.79 (*s*, 1H, 3-H). ^{13}C NMR ($CDCl_3$) δ/ppm = 198.6 (*d*, C-2).

*4.8. Aglasilvinic acid [20R,24S-epoxy-25-hydroxy-2,2-dimethoxy-2,3-secodammaran-3-oic acid] (**8**)*

Colourless oil $[\alpha]_D^{20}$ = +32° (*c* = 0.3, $CHCl_3$). IR ν cm^{-1} 3566 *w*, 2965 *s*, 2872 *m*, 1742 *m*, 1464 *m*, 1384 *m*, 1375 *m*, 1187 *w*, 1118 *m*, 1085 *w*, 1046 *m*, 952 *w*. ^{1}H NMR ($CDCl_3$, methylene and methine resonances from 2D spectra) δ/ppm = 4.68 (*br. d*, 1H, *J* = 7.0 Hz, 2-H), 3.75 (*t*, 1H, *J* = 7.3 Hz, 24-H), 3.33 (*s*, 3H, acetalic OMe), 3.22 (*s*, 3H, acetalic OMe), 2.01 (*m*, 1H, 5-H), 1.86 (*m*, 1H, 1-Ha), 1.77 (*m*, 1H, 17-H), 1.75 (*m*, 1H, 13-H), 1.70 (*m*, 1H, 9-H), 1.65 (*m*, 1H, 1-Hb), 1.23 (*s*, 3H, 29-Me), 1.22 (*s*, 3H, 28-Me), 1.21 (*s*, 3H, 26-Me), 1.15 (*s*, 3H, 21-Me), 1.11 (*s*, 3H, 27-Me), 0.98 (*s*, 3H, 18-Me), 0.92 (*s*, 3H, 19-Me), 0.87 (*s*, 3H, 30-Me). ^{1}H NMR (acetone-d_6, methylene and methine resonances from 2D spectra) δ/ppm = 4.74 (*dd*, 1H, *J* = 6.6 and 2.3 Hz, 2-H), 3.75 (*t*, 1H, *J* = 7.2 Hz, 24-H), 3.31 (*s*, 3H, acetalic OMe), 3.22 (*s*, 3H, acetalic OMe), 2.14 (*dd*, 1H, *J* = 11.8 and 2.5 Hz, 5-H), 1.86 (*m*, 1H, 1-Ha), 1.80 (*m*, 1H, 17-H), 1.82 (*m*, 1H, 13-H), 1.75 (*m*, 1H, 9-H), 1.68 (*m*, 1H, 1-Hb), 1.28 (*s*, 3H, 29-Me), 1.22 (*s*, 3H, 28-Me), 1.12 (*s*, 3H, 26-Me), 1.12 (*s*, 3H,

21-Me), 1.08 (*s*, 3H, 27-Me), 1.02 (*s*, 3H, 18-Me), 0.94 (*s*, 3H, 19-Me), 0.92 (*s*, 3H, 30-Me). EIMS $m/z = 445$ (3%), 413 (7), 395 (3), 143 (100), 85 (23). ESIMS $m/z = 559$ $[M + Na]^+$; $M = 536$ ($C_{32}H_{56}O_6$).

4.9. Pregnacetal [17α,20R-dihydroxy-3,3-dimethoxypregnan-16-one] (**9**)

Amorphous powder $[\alpha]_D^{20} = -68°$ ($c = 0.3$, $CHCl_3$). IR ν_{CCl4} cm^{-1} 3524 *m*, 2977 *s*, 2945 *s*, 2868 *s*, 1731 *s*, 1445 *m*, 1382 *m*, 1350 *w*, 1306 *w*, 1286 *w*, 1172 *w*, 1152 *w*, 1119 *s*, 1101 *w*, 1076 *w*, 1053 *m*, 1005 *w*, 931 *w*. ^1H NMR ($CDCl_3$) δ/ppm = 4.12 (*qd*, 1H, $J = 6.3$ and 1.8 Hz, 20-H), 4.03 (*br. s*, 1H, 20-OH), 3.29 (*s*, 1H, 17-OH), 3.19 (*s*, 3H, acetalic OMe), 3.14 (*s*, 3H, acetalic OMe), 2.39 (*dd*, 1H, $J = 18.8$ and 7.7 Hz, 15-Hβ), 2.13 (*m*, 1H, 14-H), 1.91 (*m*, 1H, 12-Ha), 1.89 (*m*, 1H, 2-Ha), 1.84 (*dd*, 1H, $J = 18.8$ and 12.6 Hz, 15-Hα), 1.14 (*d*, 3H, $J = 6.3$ Hz, 21-Me), 0.82 (*s*, 3H, 19-Me), 0.77 (*s*, 3H, 18-Me). EIMS $m/z = 394$ (1.5%, M^+, $C_{23}H_{38}O_5$), 348 (4), 304 (18), 288 (16), 230 (7), 84 (100).

4.10. X-ray structure analysis of silvaglin A (**1**)

The compound crystallised from ethanol by room-temperature evaporation in comparatively large brick-like orthorhombic crystals. X-ray data were collected at $T = 100$ K on a Bruker Smart APEX CCD area detector diffractometer with graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, using 0.3° ω-scan frames covering a complete sphere of the reciprocal space. After data integration, corrections for absorption and $\lambda/2$-effects were applied to the data. The structure was solved with direct methods and was then refined on F^2 with hydrogen atoms in idealized positions using the program package SHELXTL (Bruker AXS Inc., Madison, WI, USA). The absolute structure was inferred from related terpenes. A modest orientation disorder of the aldehyde group was taken into account (oxygen in two alternative positions in 82:18 proportion). Crystal data are: $C_{30}H_{48}O_4$, $M = 472.68$, orthorhombic, space group $P2_12_12_1$ (no. 19), $T = 100(2)$ K, $a = 8.4747(6)$ Å, $b = 9.4801(7)$ Å, $c = 32.633(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2621.7(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.198$ g/cm^3, $\mu = 0.077$ mm^{-1}, $F(000) = 1040$, colourless prism of $0.66 \times 0.44 \times 0.23$ mm. Of 45853 reflections collected up to $\theta_{max} = 30°$, 4294 were independent, $R_{int} = 0.031$, and 4045 were observed ($I > 2\sigma(I)$); final R indices: $R_1 = 0.0505$ ($I > 2\sigma(I)$), $wR_2 = 0.1297$ (all data). Bond lengths (Å) are: O1–C2 1.158(4), O2–C3 1.209(2), O3–C20 1.460(2), O3–C24 1.445(2), O4–C25 1.433(2), C1–C2 1.500(3), C1–C3 1.538(3), C1–C10 1.571(3), C3–C4 1.524(3), C4–C5 1.543(2), C4–C28 1.535(3), C4–C29 1.538(3), C5–C6 1.513(2), C5–C10 1.558(2), C6–C7 1.536(2), C7–C8 1.548(2), C8–C9 1.568(2), C8–C14 1.575(2), C8–C18 1.549(2), C9–C10 1.543(2), C9–C11 1.537(2), C10–C19 1.534(2), C11–C12 1.538(2), C12–C13 1.529(2), C13–C14 1.550(2), C13–C17 1.536(2), C14–C15 1.545(2), C14–C30 1.548(2), C15–C16 1.539(2), C16–C17 1.555(2), C17–C20 1.535(2), C20–C21 1.526(3), C20–C22 1.541(3), C22–C23 1.533(2), C23–C24 1.537(3), C24–C25 1.542(2), C25–C26 1.524(2), C25–C27 1.523(3). CCDC 691698 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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