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SECO-GUAIANOLIDES AND OTHER CONSTITUENTS FROM *ARTEMISIA* SPECIES

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Key Word Index—*Artemisia* species; sesquiterpenes; sesquiterpene lactones; guaianolides; seco-guaianolides; bisabolene derivative; monoterpenes; coumaric acid derivatives.

Abstract—The investigation of the aerial parts of several Mongolian *Artemisia* species afforded two new guaianolides and two seco-guaianolides, a nerolidol and a bisabolene derivative, four monoterpenes and two derivatives of *p*-coumaric acids. The structures were elucidated by spectroscopic methods and a few chemical transformations.

INTRODUCTION

From the large genus *Artemisia* many species have been investigated chemically. The diversity of this genus is reflected in the nature of the major constituents. While several species can be characterized by the occurrence of eudesmanolides and guaianolides, mostly highly oxygenated, others mainly contain coumarins or sesamine like lignanes. We have studied several species from the Mongolian Peoples Republic and the results are discussed in this paper.

RESULTS AND DISCUSSION

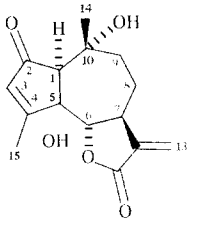
Rutifolin, which may be identical with canin, is reported from the aerial parts of *Artemisia rutifolia* Steph. ex Spreng. [1]. Material collected in the Zezerleg Mountains, Mongolia, afforded germacrene D, ar-curcumene, camphor, *cis*-verbenol, *trans*-chrysanthenol, coumarin, scopoletin, *p*-hydroxyacetophenone, 9-hydroxynerolidol, 6-oxo-5,6-seco-caryophyllen-5-al [2], the germacranolides hanphyllin [3], novanin [4] and artabin [5], the guaianolides canin [6], artecanin [6], dehydroleucodin [7], tanaparthin-α-peroxide [8], seco-tanapartholides A and B (**4**) [8], the new sesquiterpene lactones **2**, **5** and **6**, as well as the monoterpenes **8** and **10**–**12**.

EIMS of **2** as well as of the acetate **3**, obtained by mild acetylation, gave no molecular ion. However, CIMS of both compounds gave clear [M + 1] peaks and the molecular formula of **2** could be established ($C_{15}H_{20}O_6$). This formula required a lactone with three hydroxy groups if an epoxide was proposed for the structure. In the ^{1}H NMR spectrum (Table 1) all signals could be assigned by spin decoupling as the H-7 signal could be recognized by the typical splitting. However, the relative position of the hydroxy and the epoxide groups at C-1–C-4 and C-10 could not be determined directly and also the stereochemistry at these centres had to be established. Inspection of models and comparison of the coupling $J_{2,3}$ with those of similar compounds indicated that a 1,2-epoxide was present. If the chemical shifts of H-2 and H-5–H-7 were compared with those of similar lactones then H-2 and H-6 seem to be deshielded while H-5 and H-7 are not influenced by the 4- or 10-hydroxy group. Accordingly, a 4β,10α-dihydroxy derivative was most likely.

The ^{1}H NMR spectrum of **5** (Table 1) indicated the presence of a methyl ketone by the typical signal of a three proton singlet at δ2.12. Pairs of double triplets at δ2.59 and 2.54 as well as a pair of double doublet triplets at δ1.94 and 1.85 indicated a methyl ketone side chain located at C-7 as spin decoupling showed that the latter signals were coupled with H-7. Irradiation of the latter further allowed the assignment of the H-6 signal which was a doublet thus indicating the absence of a H-5 proton. The chemical shift already indicated the presence of neighbouring olefinic carbon. Accordingly, the C-4 methyl signal was at δ2.14. It showed a small homoallylic coupling with H-6. A pair of double doublets at δ2.82 and 2.31 collapsed to doublets by irradiation at δ4.72, obviously the signal of a proton under the hydroxy group. Accordingly, this broadened signal sharpened after deuterium oxide exchange. The observed couplings indicated that a β-hydroxy group was most likely.

High resolution EIMS of **6** gave the molecular formula $C_{15}H_{18}O_5$ and clear fragments were observed at *m/z* 260 $[M-H_2O]^+$, 166 (McLafferty, split of the 5,6-bond), 124 [166 − ketene]$^+$, 109 $[166-CH_2COMe]^+$, 97 $[MeCOCH{=}CHCO]^+$, 69 $[97-CO]^+$. This is in very good agreement with the partial structures which can be deduced from the ^{1}H NMR spectrum (Table 1). A pair of olefinic doublets with a 16 Hz coupling, two methyl singlets for methyl ketones at δ2.36 and 2.18 as well as clear sequences of H-5–H-9 and the presence of the exomethylene doublets (H-13) could be accomodated in the seco-lactone **6**. While **6** obviously is the product of a retro-aldol-reaction of **4** followed by *cis–trans*-isomerization, both **4** and **5** most probably are formed by oxidative cleavage of corresponding guaianolides. We have named compound **5** iso-seco-tanapartholide and **6** bis-seco-tanapartholide. Biogenetic considerations led to the proposed configuration at C-7 for all seco-compounds (**4**–**6**). In ref. [8] the stereochemistry was assigned incorrectly.

The structure of **8**, which on oxidation gave the ketone



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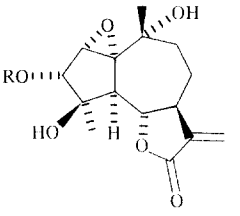
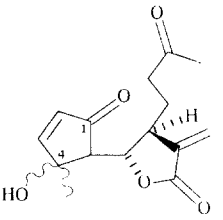


2 R = H
3 R = Ac



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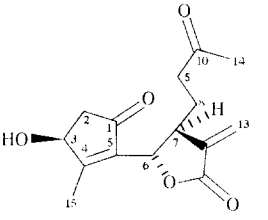

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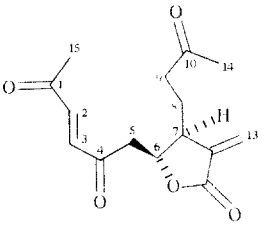

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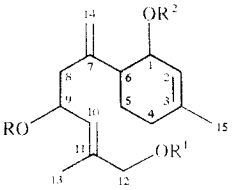
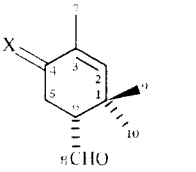
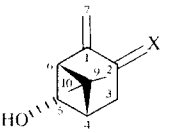


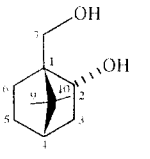
	7	7a	7b	7c
R	Ac	Ac	Ac	H
R^1	Ac	H	Ac	Ac
R^2	Ac	Ac	H	Ac



8 X = βOH,H
9 X = O



10 X = O
11 X = αOH,H



12

9, followed from the molecular formula and the ^{1}H NMR spectra (Table 2). Inspection of a Dreiding-model showed that the couplings observed agreed best with the proposed configuration and the allylic coupling of H-2 with H-4 established the relative position of the oxygen functions. Furthermore the signals in the spectrum of **9** clearly indicated the relative positions. The corresponding keto acid was reported from *Artemisia filifolia* [9]. The spectral data of **11** (Table 2) showed that a derivative of *trans*-chrysanthenol was present. The configuration at C-2 and C-5 could be deduced from the couplings. The ^{1}H NMR spectrum of **10** (Table 2) clearly showed that this compound was the corresponding 2-keto derivative of **11**. Accordingly, the exomethylene protons (H-7) were shifted downfield and the signals of H-3 now were double doublets. The ^{1}H NMR spectrum of **12** (Table 2) was close to that of borneol. However, the pair of doublets at δ3.82 and 3.67 indicated that one of the methyls was transformed to hydroxymethylene. Comparison of the chemical shifts with those of borneol indicated the relative position of the hydroxyl group. The absolute configurations of **8**–**12** were not determined.

The aerial parts of *Artemisia laciniata* Willd. also gave ar-curcumene, camphor, *trans*-chrysanthenol, coumarin, *p*-hydroxyacetophenone, scopoletin, 7-hydroxyborneol (**12**), tanaparthin-α-peroxide and seco-tanapartholide A and B (**4**) as well as eremophil-9,11-dien-12-oic acid [10], 8α-acetoxy-iso-costic acid also present in *Artemisia pectinata* [10] and 3-hydroxyocta-1,6*E*-dien-5-one [11].

The aerial parts of *Artemisia xanthochroa* Krasch. gave camphor, benzyl acetone [12], 3-hydroxybutyl-(1)-benzene [12], dehydroleucodin, hanphyllin, artecanin, canin, balchanin [13], artecanin hydrate (**2**), seco-tanapartholide A and B, iso-secotanapartholide (**5**) and the new guaianolide **1**. The molecular formula ($C_{15}H_{16}O_4$) was deduced from the $[M-H_2O]^+$ peak in the mass spectrum. From a very small peak at *m/z* 278 and a more pronounced one at *m/z* 263 $[M-Me]^+$ it was obvious that the *m/z* 260 ion was already a fragment. The ^{1}H NMR spectrum (Table 1) showed that most likely a derivative of dehydroleucodin

Table 1. ^{1}H NMR spectral data of compounds **1**–**3**, **5** and **6** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**3**	**5**	**6**
H-1	2.64 *s*	—	—	—	—
H-2	—	3.89 *d*	3.89 *d*	2.82 *dd* 2.31 *dd*	6.79 *d*
H-3	6.05 *q*	3.82 *d*	4.85 *d*	4.72 *br d*	6.83 *d*
H-5	—	2.34 *d*	2.48 *d*	—	3.15 *dd* 2.90 *dd*
H-6	4.40 *d*	4.49 *dd*	4.48 *dd*	4.97 *d*	4.68 *ddd*
H-7	3.39 *ddddd*	2.85 *ddddd*	3.02 *ddddd*	3.09 *dddt*	2.79 *dddt*
H-8α	1.8–2.0 *m*	2.20 *dddd*	2.21 *m*	1.94 *ddt*	1.91 *dddd*
H-8β		1.54 *dddd*	1.52 *m*	1.85 *ddt*	1.85 *dddt*
H-9α		1.85 *ddd*	1.88 *m*	2.59 *dt*	2.66 *dt*
H-9β		1.95 *ddd*		2.54 *dt*	2.54 *dt*
H-13	6.22 *d*	6.25 *d*	6.22 *d*	6.35 *d*	6.33 *d*
H-13′	5.71 *d*	5.54 *d*	5.50 *d*	5.67 *d*	5.69 *d*
H-14	1.56 *s*	1.29 *s*	1.25 *s*	2.12 *s*	2.18 *s*
H-15	2.27 *d*	1.44 *s*	1.40 *s*	2.14 *s*	2.36 *s*
OAc or OH	2.84 *br s* 2.72 *br s*	—	2.13 *s*	—	—

J (Hz): Compound **1**: 3,15 = 1; 6,7 = 7,8β = 10; 7,8α ~ 3; 7,13 = 3.5; 7,13′ = 3; compounds **2** and **3**: 2,3 = 2.8; 5,6 = 11.5; 6,7 = 10; 7,8α = 3; 7,8β = 11; 7,13 = 3.5; 7,13′ = 3; 8α,8β = 13; 8α,9α = 3.5; 8α,9β = 11; 8β,9α = 4; 8β,9β = 6; 9α,9β = 15; compound **5**: 2,2′ = 19; 2,3 = 6.5; 2′,3 = 2; 3,15 ~ 0.5; 6,7 = 5.5; 7,8 = 7,8′ = 7; 7,13 = 2.7; 7,13′ = 2.5; 8,8′ = 14; 8,9 = 8,9′ = 8′,9 = 8′,9′ ~ 7; 9,9′ = 16; compound **6**: 2,3 = 16; 5,5′ = 17.5; 5,6 = 5.5; 5′,6 = 7; 6,7 = 4; 7,8 = 7′,8′ = 8,9 = 8,9′ = 8′,9 = 8′,9′ = 7; 7,13 = 2.5; 7,13′ = 2; 8,8′ = 14; 9,9′ = 18.

Table 2. ^{1}H NMR spectral data of compounds **8**–**12** (400 MHz, $CDCl_3$, TMS as internal standard)

	8	**9**	**10**	**11**	**12**
H-2	5.13 *dq*	6.32 *q*	—	4.36 *br d*	4.45 *ddd*
H-3	—	—	α 2.52 *dd* β 2.68 *dd*	α 1.93 *br dd* β 2.35 *ddd*	α 0.95 *dd* β 2.28 *m*
H-4	4.08 *br t*	—	2.41 *dddd*	2.30 *m*	1.62 *t*
H-5	α 1.78 *ddd* β 2.21 *ddd*	α 2.64 *dd* β 2.57 *dd*	4.69 *t*	4.45 *br t*	α 1.41 *m* β 1.81 *m*
H-6	2.40 *ddd*	2.85 *ddd*	3.04 *t*	2.92 *t*	α 2.28 *m* β 1.33 *m*
H-7	1.75 *br s*	1.77 *d*	6.14 *d* 5.13 *d*	5.18 *br s* 4.99 *br s*	3.82 *d* 3.67 *d*
H-8	9.83 *d*	9.86 *d*	—	—	—
H-9	1.18 *s*	1.41 *s*	0.81 *s*	0.67 *s*	0.89 *s*
H-10	1.05 *s*	1.17 *s*	1.28 *s*	1.18 *s*	0.87 *s*

J (Hz): Compound **8**: 2,4 = 2,7 = 1; 4,5α = 7.5; 4,5β = 6; 5α,5β = 14; 5α,6 = 10; 5β,6 = 3; 6,8 = 2; compound **9**: 2,7 = 1.5; 5α,5β = 17; 5α,6 = 11; 5β,6 = 5; 6,8 = 1.5; compound **10**: 3α,3β = 19; 3α,4 = 3; 3β,4 = 3.3; 4,5 = 4,6 = 5,6 ~ 6; compound **11**: 2,3β = 8.5; 2,7 = 2,7′ ~ 0.5; 3α,3β = 15; 3α,4 = 4; 3β,4 = 2; 4,5 = 4,6 = 5,6 = 5.5; 7,7′ ~ 0.5; compound **12**: 2,3α = 3.5; 2,3β = 10; 3α,3β = 13.5; 2,6 = 2; 3β,4 = 4,5β = 5; 5α,5β = 6α,6β = 14; 7,7′ = 10.

was present where a hydroxy group was at C-5. Accordingly, the H-6 signal was simply a doublet. Furthermore, one of the olefinic methyls of dehydroleucodin was replaced by an upfield shifted methyl singlet at δ1.56. As the H-3 signal was still an olefinic one, which showed an allylic coupling with a doublet at δ2.27, the 1(10)-double bond was hydrated. Thus the new lactone was a 5,10-dihydroxyguaianolide with a keto group at C-2 and a 3,4-double bond. The configuration at C-5 could not be determined with certainty. The stereochemistry at C-10 was determined by NOE difference spectroscopy. Clear NOEs were observed between H-14 and H-6 and between

H-7 and H-9α and H-1. Thus **1** is 5β,10α-dihydroxy-1α-H-dehydroleucodin.

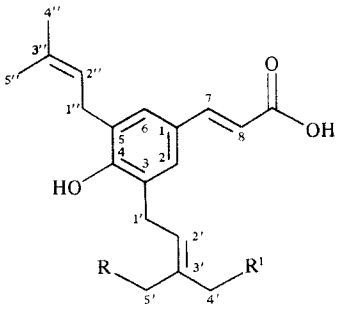
The aerial parts of *Artemisia schischkinii* Krasch. contain farnesyl isovalerate, arborescin [14, 15] and ashantin, present in many other *Artemisia* species [16]. The aerial parts of *Artemisia patustris* L. gave germacrene D, caryophyllene, dehydrofalcarinol [17] also present in the roots, *p*-hydroxyacetophenone and the *p*-coumaric acid derivative **13** [18] as well as the isomeric hydroxy derivatives **14** and **15**. While the latter was obtained pure, **14** only could be isolated as its methyl ester **14a**. Compound **15a** also was transformed to **16** by treatment with acid. The structures of **14** and **15** followed from the ^{1}H NMR spectra (Table 3) which were close to that of **13** [18] which further showed that **14a** and **15b** only differed in the position of the hydroxy group. In the spectrum of **14a** the signal of the olefinic proton (H-2′) was shifted down field if compared with the shift of the same proton in the spectrum of **15a**, thus the isomer **14a** was assigned the *E*-configuration. Similar isomers of the corresponding *p*-hydroxyacetophenones were isolated from *Artemisia campestris* showing the same differences in the NMR spectra [19].

The aerial parts of *Artemisia stelleriana* Bess. gave as reported previously the thiophene enolether spiroketal with a six membered ring [17] and sesquiphellandrene as well as the triacetate **7**. The mass spectrum gave the molecular formula $C_{21}H_{30}O_6$ and showed a base peak at *m/z* 84, obviously the result of a RDA and loss of ketene. While the positions of the acetoxy groups at C-1 and C-9 directly followed from the ^{1}H NMR spectrum (Table 4) the position of the last oxygen function could not be assigned directly. Partial saponification gave three diacetates (**7a–7c**). The position of the free hydroxy was deduced in each case from the ^{1}H NMR spectrum (Table 4). The clear upfield shift of the H-13 signal in the spectrum of **7c** could be explained only by the changed nature of the oxygen function at C-9. However, this requires an *E*-configuration of the Δ^{10}-double bond. Dihydrosantonin, which was reported previously [20] from this species, was not isolated.

Table 3. ^{1}H NMR spectral data of compounds **14a**, **15**, **15a** and **16** (400 MHz, $CDCl_3$, TMS as internal standard)

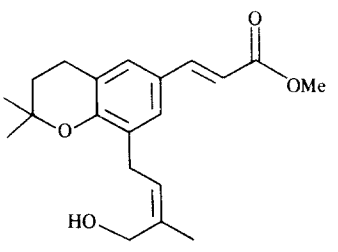
	14a	15	15a	16
H-2	7.16 *br s*	7.19 *d*	7.14 *d*	7.13 *d*
H-6		7.20 *d*	7.16 *d*	7.11 *d*
H-7	7.59 *d*	7.69 *d*	7.59 *d*	7.58 *d*
H-8	6.27 *d*	6.28 *d*	6.26 *d*	6.26 *d*
H-1′	3.37 *br d*	3.46 *br d*	3.43 *br d*	3.34 *br d*
H-2′	4.07 *br s*	5.40 *br t*	5.38 *br t*	5.41 *br t*
H-4′	5.58 *tq*	1.82 *s*	1.79 *d*	1.83 *br d*
H-5′	1.79 *br s*	4.37 *s*	4.30 *br s*	4.24 *br s*
H-1″	3.33 *br d*	3.33 *br d*	3.30 *br d*	2.77 *br t*
H-2″	5.28 *tqq*	5.31 *br t*	5.30 *tqq*	1.81 *t*
H-4″	1.78 *br s*	1.74 *br s*	1.76 *d*	1.59 *s*
H-5″	1.79 *br s*	1.78 *br s*	1.72 *br s*	
OMe	3.78 *s*	—	3.78 *s*	3.77 *s*
OH	5.69 *br s*		7.49 *br s*	
			2.67 *br s*	

J (Hz): 2,6 = 1.7; 2,1′ = 6,1″ ~ 1; 7,8 = 16; 1′,2′ = 1″,2″ = 7.5; 2′,4′ = 2′,5′ = 2″,4″ = 2″,5″ ~ 1 (compound **16**:6,1′ ~ 1; 1″,2″ = 7).



	13*	14*	15*
R	H	H	OH
R^1	H	OH	H

***13a-15a** are the corresponding methyl esters



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The results on Mongolian *Artemisia* species discussed here and in some previous papers [10, 21, 22] showed again that the chemistry of this large genus may help in the classification of the different sections and groups. The accumulation of guaianolides, especially highly oxygenated ones, obviously is characteristic for a group of East Asian species. However, these compounds are not present in all species so far investigated. As in other areas of the world obviously chemically diverse groups, most likely belonging to different sections, can be recognized. So far it has been shown that sesquiterpene lactones [23], acetylenes [17, 24, 25], oxygenated coumarins and sesamine-like compounds [26] are widespread in the genus. However, no clear agreement with proposed divisions of the genus is observable. Still more species have to be studied chemically and also taxonomic investigations are desirable.

EXPERIMENTAL

The plant material was extracted at room temp. with MeOH–Et_2O–petrol (1:1:1) and the extracts obtained were separated as reported previously [27].

The extract from the aerial parts (570 g) of *Artemisia rutifolia* (voucher 56, collected in the Mongolian Peoples Republic, Bulgan Aimak, Chögno Tarna Uul (Zezerleg Mountains)) was separated by CC (silica gel) affording seven fractions [Fr. 1: petrol and Et_2O–petrol (1:20), Fr. 2: Et_2O–petrol, (1:10), Fr. 3: Et_2O–petrol (1:3), Fr. 4: Et_2O–petrol (1:1), Fr. 5: Et_2O, Fr. 6: Et_2O–MeOH (9:1) and Fr. 7: Et_2O–MeOH (4:1)]. TLC (always

Table 4. ^{1}H NMR spectral data of compounds 7 and 7a–7c (400 MHz, $CDCl_3$, TMS as internal standard)

	7				
	$CDCl_3$–C_6D_6	$CDCl_3$	7a	7b	7c
H-1	5.46 *br d*	5.51 *br d*	5.62 *br d*	4.41 *br d*	5.51 *br d*
H-2	5.03 *br d*	5.15 *br d*	5.19 *br d*	5.23 *br d*	5.13 *br d*
H-4	2.25 *br d*	2.40 *br d*	2.39 *br d*	2.41 *br d*	2.39 *br d*
H-4′	1.47 *dd*	*	*	*	*
H-5	1.69 *m*	*	*	*	*
H-5′	1.85 *m*	*	*	*	*
H-6	1.96 *br d*	*	2.12 *br d*	*	*
H-8	2.45 *dd*	2.58 *dd*	2.59 *dd*	2.58 *dd*	2.59 *dd*
H-8′	2.09 *dd*	2.20 *dd*	2.20 *dd*	2.22 *dd*	2.12 *dd*
H-9	5.55 *ddd*	5.64 *ddd*	5.65 *ddd*	5.63 *ddd*	4.67 *ddd*
H-10	4.93 *br d*	5.06 *br d*	5.07 *br d*	5.07 *br d*	5.10 *br d*
H-12	4.54 *d*	4.63 *d*	4.14 *br s*	4.65 *d*	4.62 *d*
H-12′	4.46 *d*	4.56 *d*		4.55 *d*	4.54 *d*
H-13	1.69 *br s*	1.80 *br s*	1.80 *br s*	1.79 *br s*	1.72 *br s*
H-14	5.09 *br s*	5.20 *br s*	5.16 *br s*	5.29 *br s*	5.20 *br s*
H-!4′	4.96 *br s*	5.08 *br s*	4.98 *br s*	5.18 *br s*	5.09 *br s*
H-15	1.44 *br s*	1.58 *br s*	1.60 *br s*	1.53 *br s*	1.56 *br s*
1-OAc	1.82 *s*	1.99 *s*	1.99 *s*	—	1.99 *s*
9-OAc	1.85 *s*	2.03 *s*	2.03 *s*	2.04 *s*	—
10-OAc	1.86 *s*	2.06 *s*	—	2.09 *s*	2.06 *s*

*Obscured multiplets.

J (Hz): 1,2 = 7; 4,4′ = 15; 4′,5 = 4; 5′,6 = 6; 8,8′ = 12; 8,9 = 5.5; 8′,9 = 9,10 = 10.5; 12,12′ = 13.5.

silica gel, PF 254) of fraction 1 (petrol) gave 2 mg germacrene D and 3 mg ar-curcumene (identified by GCMS). Fraction 2 gave nothing of interest. TLC of fraction 3 (Et_2O–petrol, 1:9) gave 3 mg camphor and 8 mg *trans*-chrysanthenol. TLC of fraction 4 (Et_2O–petrol, 1:1) gave two bands (4/1 and 4/2). TLC of 4/1 (Et_2O–petrol, 1:1) gave 5 mg camphor and 12 mg *trans*-chrysanthenol and TLC of 4/2 (Et_2O–petrol, 1:1, two developments) gave 10 mg *cis*-verbenol, 10 mg coumarin and a mixture ($R_f \sim 0.45$), which together with 5/1 (see below) was separated by HPLC (MeOH–H_2O, 7:3, always RP 8, *ca* 120 bar, flow rate, 3 ml/min) affording 10 mg *p*-hydroxyacetophenone (R_t 0.8 min), 6 mg **8** (R_t 1.6 min), 2 mg novanin (R_t 3.2 min), 3 mg 9-hydroxynerolidol (R_t 4.7 min) and 3 mg 6-oxo-5,6-seco-caryophyllen-5-al (R_t 5.5 min). TLC of fraction 5 (Et_2O–petrol, 3:1) gave four bands (5/1–5/4). HPLC (MeOH–H_2O, 3:2) of 5/2 (R_f 0.55) gave 5 mg *p*-hydroxyacetophenone (R_t 1.5 min), 2 mg **10** (R_t 2.5 min) and 2 mg **11** (R_t 4.6 min). HPLC (MeOH–H_2O, 3:2) of 5/3 (R_f 0.4) gave 12 mg tanaparthin-α-peroxide (R_t 1.4 min) and a mixture (R_t 4.0 min) which was separated by TLC (Et_2O–C_6H_6–$CHCl_3$, 1:1:1) affording 2 mg dehydroleucodin (R_f 0.52), 3 mg hanphyllin (R_f 0.40) and 10 mg **12** (R_f 0.30). HPLC (MeOH–H_2O, 3:2) of 5/4 (R_f 0.2) gave 2 mg artabin (R_t 3.8 min). TLC of fraction 6 (Et_2O) gave 100 mg scopoletin (R_f 0.55) and a mixture (R_f 0.3) which was separated by HPLC (MeOH–H_2O, 1:1) affording a mixture (R_t 1.5 min) which gave by TLC (Et_2O–C_6H_6–$CHCl_3$, 1:1:1) 5 mg **6** (R_f 0.64) and a mixture (R_f 0.4) which by TLC (Et_2O–petrol, 3:1, and than Et_2O) gave 5 mg canin (R_f 0.32) and 10 mg seco-tanapartholides A and B (**4**) (R_f 0.28). Fraction 7 was further separated by medium pressure CC (silica gel Woelm, 32–63, 25 ml fractions). Fractions 5–10 (Et_2O) gave 50 mg scopoletin, fractions 11–14 (Et_2O–MeOH, 99:1) afforded by TLC (Et_2O–MeOH, 99:1) 10 mg scopoletin (R_f 0.62) and 4 mg artecanin (R_f 0.45). Fractions 15–25 (Et_2O–MeOH, 19:1) gave by TLC (Et_2O–MeOH, 99:1) 10 mg scopoletin and a mixture (R_f 0.45) which was combined with fractions 26–33 (Et_2O–MeOH, 9:1) which by TLC (Et_2O–MeOH, 99:1) gave 10 mg seco-tanapartholide A and B (**4**) and 30 mg canin. Fractions 34–40 (Et_2O–MeOH, 5:1) gave by TLC (Et_2O–MeOH, 97:3) four bands (7/1–7/4). Band 7/1 gave 10 mg scopoletin, 7/2 5 mg artecanin, 7/3 20 mg seco-tanapartholides A and B (**4**). TLC of 7/4 (Et_2O–MeOH, 9:1) gave a mixture (R_f 0.6) which by HPLC (MeOH–H_2O, 2:3) gave 2 mg **2** (R_t 1.1 min) and a mixture (R_t 1.8 min) which by TLC (Et_2O–MeOH, 9:1) gave 2 mg **5** (R_f 0.65). The amounts of the seco-tanapartholides and of **5** were much higher in the crude fractions, but the compounds were destroyed to a large extent during the separations.

The extract of the aerial parts (440 g) of *Artemisia laciniata* (voucher 46) collected in the Mongolian Peoples Republic, Bulgan Aimak, 15 km E of Chutag, July 1983) gave by CC five fractions: Fr. 1 (petrol), Fr. 2 (Et_2O–petrol, 1:10), Fr. 3 (Et_2O–petrol, 9:1), Fr. 4 (Et_2O–petrol, 1:1) and Fr. 5 (Et_2O and Et_2O–MeOH, 9:1). TLC (petrol) of fraction 1 gave 10 mg ar-curcumene. TLC of fraction 2 (Et_2O–petrol, 1:20) after addition of CH_2N_2 gave 100 mg methyleremophil-9,11-dien-12-oate, 50 mg camphor and 20 mg *trans*-chrysanthenol. TLC of fraction 3 (Et_2O–petrol, 1:3) gave 20 mg coumarin and fraction 4 gave by TLC (Et_2O–petrol, 1:1) 10 mg *p*-hydroxyacetophenone and two bands (4/1 and 4/2). Band 4/1 gave after addition of CH_2N_2 by TLC (Et_2O–petrol, 1:3) 20 mg methyl-8α-acetoxy iso-costic acid ester (R_f 0.68). TLC of band 4/2 (C_6H_6–$CHCl_3$–Et_2O, 2:2:1) gave 20 mg tanaparthin-α-peroxide (R_f 0.6), 10 mg 3-hydroxyocta-1,6*E*-dien-5-one (R_f 0.45) and 20 mg 7-hydroxyborneol (R_f 0.3). TLC of fraction 5 (CH_2Cl_2–MeOH, 30:1) gave 30 mg scopoletin (R_f 0.6) and 300 mg **4** (R_f 0.45).

The extract of the aerial parts (300 g) of *Artemisia xanthochroa* (voucher 30) collected in the Mongolian Peoples Republic, Bulgan (Aimak, 15 km E of Chutag, July 1983) gave three CC fractions: Fr.

1 (Et_2O–petrol, 1:10), Fr. 2 (Et_2O) and Fr. 3 (Et_2O–MeOH, 20:1). Distillation of fraction 1 gave 100 mg camphor and 500 mg benzylacetone. TLC of fraction 2 (Et_2O–petrol, 1:1) gave three bands (2/1–2/3). TLC of 2/1 (Et_2O–petrol, 1:1) gave 100 mg 3-hydroxybutyl-1-benzene (R_f 0.56). TLC of 2/2 ($CHCl_3$–C_6H_6–Et_2O, 2:2:1) gave 200 mg dehydroleucodin (R_f 0.58) and TLC of 2/3 ($CHCl_3$–C_6H_6–Et_2O, 2:2:1) gave 200 mg dehydroleucodin (R_f 0.58) and TLC of 2/3 ($CHCl_3$–C_6H_6–Et_2O, 2:2:1) gave two bands (2/3/1 and 2/3/2). TLC of 2/3/1 (Et_2O–petrol, 3:1, two developments) gave 2 mg balchanin (R_f 0.50). TLC of 2/3/2 (same solvent) gave 100 mg hanphyllin (R_f 0.32), crude **1** which on TLC (Et_2O–petrol, 3:1, two developments) gave 5 mg **1** (R_f 0.42). TLC of fraction 3 (Et_2O–MeOH, 200:1) gave a polar band which on TLC (first $CHCl_3$–C_6H_6–Et_2O–MeOH, 7:7:7:1, then CH_2Cl_2–MeOH, 20:1) gave 2 mg canin (R_f 0.68), 4 mg artecanin (R_f 0.66), 10 mg **4** (R_f 0.58), 20 mg **5** (R_f 0.45) and 10 mg **2** (R_f 0.30). Again the lengthy separation caused considerable losses of the unstable lactones which were present in much higher concentration in the crude fractions.

The extract of the aerial parts (66 g) of *Artemisia schischkinii* (voucher 36, collected in the Mongolian Peoples Republic, Töw Aimak, Möngönmort Somon, Kerulen Valley, August 1983) gave by CC and TLC 50 mg farnesyl isovalerate (Et_2O–petrol, 1:10), 100 mg arborescin (Et_2O–petrol, 1:1, R_f 0.65) and 50 mg ashantin (Et_2O–petrol, 1:1, R_f 0.22).

The extract of the aerial parts (850 g) of *Artemisia palustris* (voucher 55, collected in the Mongolian Peoples Republic, Töw Aimak, Möngönmort Somon, Chentej Mountains, August 1983) gave four CC fractions: Fr. 1 (petrol), Fr. 2 (Et_2O–petrol, 1:3 and 1:1), Fr. 3 (Et_2O) and Fr. 4 (Et_2O–MeOH, 10:1). TLC of fraction 1 (petrol) gave 10 mg germacrene D and 10 mg caryophyllene. TLC of fraction 2 (Et_2O–petrol, 1:10) afforded 10 mg dehydrofalcarinol. Medium pressure CC (silica gel, ϕ 60 μ) of fraction 3 gave five fractions (3/1–3/5) starting with Et_2O–petrol, 1:3, 1:1 and finally Et_2O. Fraction 3/1 gave 40 mg **13**, fraction 3/2 5 mg dehydrofalcarinol, 3/3 60 mg *p*-hydroxyacetophenone, 3/4 gave 100 mg crude **14** and 3/5 100 mg **15**. Fraction 4 showed absence of OMe groups in the ^1H NMR and therefore was treated with CH_2N_2. TLC (Et_2O–petrol, 1:1) gave 20 mg **15a** (R_f 0.62), a mixture of **14a** and **15a** as well as 150 mg **14a** (R_f 0.45).

The extract of the aerial parts (220 g) of *Artemisia stelleriana* (voucher 84/1711, Botanical Garden, Berlin) gave three CC fractions. Fraction 1 (petrol) gave by TLC (petrol) 20 mg sesquiphellandrene. TLC of fraction 2 (Et_2O–petrol, 1:20) gave as previously [17] the thiophene spiroketal enolether and fraction 3 gave by TLC (Et_2O–petrol, 1:1) 40 mg **7** (R_f 0.61).

5β,10α-Dihydroxy-1α-H-dehydroleucodin (**1**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 278 $[M]^+$ (3), 263 $[M-Me]^+$ (15), 260.105 $[M-H_2O]^+$ (40) (calc. for $C_{15}H_{16}O_4$: 260.105), 242 $[260-H_2O]^+$ (38), 167 (100), 112 (81), 111 (96), 109 (72).

Artecaninhydrate (**2**). Colourless crystals, mp 142°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 278 $[M-H_2O]^+$ (11), 260 $[278-H_2O]^+$ (21), 129 (100); CIMS *m/z* (rel. int.): 297 $[M+1]^+$ (21), 279 $[297-H_2O]^+$ (100), 261 $[279-H_2O]^+$ (32), 243 $[261-H_2O]^+$ (12). To 5 mg **2** in 2 ml $CHCl_3$ 10 mg 4-pyrrolidinopyridin and 0.1 ml Ac_2O were added. After 3 hr at 20° TLC (Et_2O) gave 3 mg **3**; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1740, 1250 (OAc); EIMS *m/z* (rel. int.): 339 $[M+1]^+$ (40), 321 $[339-H_2O]^+$ (95), 261 $[321-HOAc]^+$ (100), 243 $[261-H_2O]^+$ (66); $[\alpha]_D = -22°$ ($CHCl_3$; *c* 0.44).

Iso-seco-tanapartholide (**5**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone), 1715 (C=O); MS *m/z* (rel. int.): 278.115 $[M]^+$ (2) (calc. for $C_{15}H_{18}O_5$: 278.115), 260 $[M-H_2O]^+$ (11), 218 $[260-ketene]^+$ (11), 217 $[260-MeCO]^+$ (12), 61 (100).

Bis-seco-tanapartholide (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone), 1720 (C=O); MS *m/z* (rel. int.): 278.115 $[M]^+$ (3) (calc. for $C_{15}H_{18}O_5$: 278.115), 260 $[278-H_2O]^+$ (20), 166 $[M-MeCOCH{=}CHCOMe, McLafferty]^+$ (51), 124 $[166-ketene]^+$ (51), 109 $[166-CH_2COMe]^+$ (54), 97 $[MeCOCH{=}CHCO]^+$ (100), 69 $[97-CO]^+$ (38).

1,9,12-Triacetoxybisabolene (**7**). Colourless crystals, mp 82°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1240 (OAc); MS *m/z* (rel. int.): 378.204 $[M]^+$ (0.2) (calc. for $C_{21}H_{30}O_6$: 378.204), 319 $[M-OAc]^+$ (2.5), 318 $[M-HOAc]^+$ (0.5), 258 $[318-HOAc]^+$ (22), 198 $[258-HOAc]^+$ (60), 183 $[198-Me]^+$ (67), 84 $[C_5H_8O, RCO-ketene]^+$ (100); $[\alpha]_D = -55°$ ($CHCl_3$; *c* 4.6). To 50 mg **7** in 3 ml MeOH 100 mg K_2CO_3 in 2 ml H_2O was added. After 15 min at 25° dil. H_2SO_4 was added. TLC (Et_2O– petrol, 3:1) gave 35 mg **7**, 2 mg **7b** (R_f 0.51), 3 mg **7a** (R_f 0.46) and 3 mg **7c** (R_f 0.38).

Compound **7a**. MS *m/z* (rel. int.): 336 $[M]^+$ (0.3), 277 $[M-OAc]^+$ (2), 276 $[M-HOAc]^+$ (1), 258 $[276-H_2O]^+$ (0.5), 234 $[276-ketene]^+$ (2), 216 $[276-HOAc]^+$ (24), 198 $[216-H_2O]^+$ (12), 183 $[198-Me]^+$ (22), 84 $[C_5H_8O]^+$ (100); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1740, 1245 (OAc).

Compound **7b**. MS *m/z* (rel. int.): 276 $[M-HOAc]^+$ (2.5), 216 $[276-HOAc]^+$ (8), 201 $[216-Me]^+$ (5), 198 $[216-H_2O]^+$ (6), 183 $[198-Me]^+$ (8), 84 $[C_5H_8O]^+$ (100).

Compound **7c**. MS *m/z* (rel. int.): 336 $[M]^+$ (0.6), 276 $[M-HOAc]^+$ (10), 216 $[276-HOAc]^+$ (21), 201 $[216-Me]^+$ (14), 198 $[216-H_2O]^+$ (12), 84 $[C_5H_8O]^+$ (100).

6-Formyl-1,1,3-trimethylcyclohex-2-en-4β-ol (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 2730, 1735 (CHO); MS *m/z* (rel. int.): 168.115 $[M]^+$ (0.5) (calc. for $C_{10}H_{16}O_2$: 168.115), 153 $[M-Me]^+$ (2), 150 $[M-H_2O]^+$ (3), 135 $[153-CO]^+$ (2), 122 (24), 107 (100), 91 (31). 5 mg **8** in 3 ml Et_2O were stirred 1 hr with 50 mg MnO_2. TLC (Et_2O–petrol, 1:3) gave 3 mg **9** (R_f 0.45); colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720, 1720 (CHO), 1680 (C=CC=O); MS *m/z* (rel. int.): 166 $[M]^+$ (14), 151 $[M-Me]^+$ (24), 137 $[M-CHO]^+$ (84), 109 (100); $[\alpha]_D = -25°$ ($CHCl_3$; *c* 0.3).

5α-Hydroxy-β-pinen-2-one (**10**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1710, 1630 (C=CC=O); MS *m/z* (rel. int.): 166.099 $[M]^+$ (5) (calc. for $C_{10}H_{14}O_2$: 166.099), 137 $[M-CHO]^+$ (11), 91 (100).

2α,5α-Dihydroxy-β-pinene (**11**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3595 (OH), 910 (C=CH_2); MS *m/z* (rel. int.): 168.115 $[M]^+$ (7) (calc. for $C_{10}H_{16}O_2$: 168.115), 150 $[M-H_2O]^+$ (22), 135 $[150-Me]^+$ (28), 121 $[150-CHO]^+$ (71), 107 (100), 105 (84), 91 (88).

7-Hydroxyborneol (**12**). Colourless crystals, mp 180°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620, 3450 (OH); MS *m/z* (rel. int.): 152.120 $[M-H_2O]^+$ (1) (calc. for $C_{10}H_{16}O$: 152.120), 137 $[152-Me]^+$ (4.5), 119 $[137-H_2O]^+$ (6), 108 $[152-C_2H_4O]^+$ (100), 95 (56).

3-[4′-Hydroxyprenyl]-5-prenyl-p-coumaric acid (**14**). The crude acid was transformed to methyl ester **14a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1720, 1635, 1600 (PhC=CCO_2R); MS *m/z* (rel. int.): 330.183 $[M]^+$ (32) (calc. for $C_{20}H_{26}O_4$: 330.183), 312 $[M-H_2O]^+$ (100), 297 $[312-Me]^+$ (61), 257 $[312-C_4H_7]^+$ (26), 243 (20), 206 (30).

3-[5′-Hydroxyprenyl]-5-prenyl-p-coumaric acid (**15**). Colourless crystals, mp 146°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550–2700, 1695, 1635, 1600 (PhC=CCO_2H, OH); MS *m/z* (rel. int.): 316.167 $[M]^+$ (61) (calc. for $C_{19}H_{24}O_4$: 316.167), 298 $[M-H_2O]^+$ (100), 283 $[298-Me]^+$ (95), 243 (37); To 20 mg **15** in 3 ml Et_2O excess of CH_2N_2 was added. TLC (Et_2O–petrol, 1:1) gave 20 mg **15a** (R_f 0.62); colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1720, 1630, 1600 (PhC=CCO_2R); MS *m/z* (rel. int.): 330.183 $[M]^+$ (64) (calc. for $C_{20}H_{26}O_4$: 330.183), 312 $[M-H_2O]^+$ (100), 297 $[312-Me]^+$ (24).

Compound **15a** (20 mg) was heated in C_6H_6 with 5 mg *p*-toluene sulphonic acid for 5 min at 80°. TLC (Et_2O–petrol, 1:1) gave 2 mg **15a** and 15 mg **16**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600

(OH), 1720, 1630, 1600 (PhC=CCO_2R); MS *m/z* (rel. int.): 330.183 $[M]^+$ (100) (calc. for $C_{20}H_{26}O_4$: 330.183), 312 $[M-H_2O]^+$ (22), 297 $[312-Me]^+$ (41), 257 $[312-C_4H_7]^+$ (66), 243 (24).

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