(H-15b, *br s*), 0.99 (3H-14, *s*); (C_6D_6–Me_2CO-d_6, 10:1): δ6.39 (H-13b), 6.31 (H-1), 6.18 (H-15a, *dd*, $J_{5,15a} \approx 2.0$, $J_{15a,15b} \approx 1.7$ Hz), 5.95 (H-2), 5.84 (C12-OH, *br s*), 5.42 (H-13a), 4.91 (H-15b), 0.71 (3H-14); (Me_2CO-d_6): δ6.91 (H-1), 6.17 (H-13b), 5.92 (H-15a), 5.87 (H-2), 5.70 (H-13a), 5.16 (H-15b), 1.00 (3H-14); MS *m/z* (rel. int.): 247.9 (6), 247.0 (18), 246.0 $[M]^+$, $C_{15}H_{18}O_3$ (19), 230.9 $[M-Me]^+$ (10), 228 $[M-H_2O]^+$ (11), 213.0 (6), 200.9 (11), 199.9 (8), 173.0 (9), 159.0 (9), 135.1 (13), 91.0 (25), 43.1 (20), 41.0 (21), 31.9 (33), 28 (100); CIMS (isobutane) *m/z* (rel. int.): 247.1 $[M+1]^+$ (100), 229 $[M+1-H_2O]^+$ (8).

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CLERODANE DITERPENOIDS FROM *ASTER ALPINUS*

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Key Word Index—*Aster alpinus*; Compositae; diterpenes; clerodane derivatives.

Abstract—The aerial parts of *Aster alpinus* afforded, in addition to dammadienyl acetate and dammadienone, two clerodane derivatives related to salviarin and bacchotricuneatin A. The structures were elucidated by spectroscopic methods, especially high-field NMR. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

From the large genus *Aster* (Compositae, tribe Astereae) several species have already been studied. In addition to acetylenic compounds [1, 2], umbelliferone derivatives of sesquiterpenes may be characteristic of some groups [3]. So far, only one species has given sesquiterpene lactones [4]. We have now studied *Aster alpinus* L. Only some unusual fatty acids [5] and, from the roots, lachnophyllum ester [1] were reported from this species. The results are discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts of the widespread perennial *Aster alpinus* L., collected in the Mongolian Peoples Republic, afforded dammadienyl acetate and dammadienone as well as two diterpenes, the clerodane derivatives **1** and **2**.

The molecular formula of **1** was $C_{25}H_{28}O_8$ and the loss of 99 mu and a strong fragment at *m/z* 83 ($C_4H_7CO^+$) indicated the presence of an unsaturated C_5-ester. The ^1H NMR spectrum (Table 1) showed that this ester group was an angelate as followed from the typical signals (δ6.16 *qq*, 2.03 *dq* and 1.85 *dq*). Furthermore, characteristic signals of a β-substituted furan could be recognized. A pair of doublets at δ3.85 and 4.66 indicated an oxygen-bearing methylene group, most likely part of a γ-lactone, its presence also being indicated by the IR spectrum. A slightly broadened double-doublet at δ5.30 was coupled with one of the furan protons. Accordingly, this signal could be assigned to H-12, which must be located at an oxygen-bearing carbon. Spin decoupling, especially in deuteriobenzene, allowed the assignment of all signals. The sequences obtained were interrupted by two quaternary carbons and by carbonyl groups. However, a W-coupling between H-19α and H-6 indicated the connection between the two sequences and showed that C-5 was quaternary. As the singlet at δ2.63 showed a weak W-coupling with H-20 and only H-8 was coupled with H-7, the remaining groups had to be placed in a clerodane skeleton. The stereochemistry was supported by a W-coupling between H-2β and H-4, by the magnitude of the couplings of H-6, H-8 and H-12, and by NOE difference spectroscopy. Irradiation of H-20 caused clear NOEs with H-11β (7%), H-8 (6%), H-19α (6%), H-19β (3%) and H-12 (1.5%). Furthermore, NOEs between H-8 and H-12 (10%) and between H-4 and H-6 (10%) were observed. Inspection of models showed that this could be expected only if ring C was in a boat form, obviously due to the β-substituent at C-12 which would be axial in a chair form. The small coupling of H-4 also required a boat conformation for ring A. This is possibly due to some steric hindrance between C-18 and the angelate residue which

Table 1. ^{1}H NMR and ^{13}C NMR spectral data of 1 and 2 (400 MHz, TMS as internal standard)

	^{1}H NMR			^{13}C NMR ($CDCl_3$)	
	1 ($CDCl_3$)	1 (C_6D_6)	2* ($CDCl_3$)		1
H-2α	2.14 *ddd*	1.67 *m*	2.31 *m*	C-1	207.3 *s*
H-2β	2.50 *ddd*	1.82 *ddd*	2 52 *m*	C-2	46.9 *t*
H-3α	2.30 *m*	1.74 *m*	7.10 *dd*	C-3	21.7 *t*
H-3β	2.23 *m*	1.19 *m*		C-4	44.3 *d*
H-4	2.84 *ddd*	2.64 *br d*		C-5	45.5 *s*
H-6	5.47 *dd*	5.57 *dd*	4.36 *d*	C-6	73.1 *d*
H-7α	1.85 *m*	1.19 *m*	6.66 *d*	C-7	23.7 *t*
H-7β	2.65 *m*	2.53 *ddd*		C-8	45.3 *d*
H-8	2.68 *br d*	1.67 *dd*	—	C-9	34.5 *s*
H-10	2.63 *s*	2.25 *s*	2.61 *dd*	C-10	58.2 *d*
H-11α	1.79 *dd*	1.63 *dd*	2.06 *dd*	C-11	37.1 *t*
H-11β	2.58 *dd*	2.37 *dd*	2.21 *dd*	C-12	70.4 *d*
H-12	5.30 *br dd*	4.62 *br dd*	5.17 *br dd*	C-13	123.2 *s*
H-14	6.40 *dd*	6.21 *dd*	6.42 *dd*	C-14	108.5 *d*
H-15	7.40 *dd*	7.08 *dd*	7.43 *dd*	C-15	143.7 *d*
H-16	7.47 *br s*	7.18 *br s*	7.48 *br s*	C-16	139.9 *d*
H-19α	3.85 *br d*	3.37 *br d*	3.99 *d*	C-17	172.1 *s*
H-19β	4.66 *d*	4.20 *d*	4.01 *d*	C-18	177.9 *s*
H-20	1.34 *s*	0.72 *s*	0.99 *s*	C-19	70.8 *t*
OCOR	6.16 *qq*	5.79 *qq*	—	C-20	22.8 *q*
	2.03 *dq*	2.11 *dq*	—	C-1′	166.1 *s*
	1 85 *dq*	1.98 *dq*	—	C-2′	126.7 *s*
				C-3′	141.1 *d*
				C-4′	20.3 *q*
				C-5′	16.9 *q*

*H-1, 1.30 *m*, 1.83 *br d*.

J (Hz): compound **1**: 2α, 2β = 18; 2α, 3α = 4; 2α, 3β = 12; 2β, 3α = 2; 2β, 3β = 3; 2β, 4 = 1.5; 3α, 4 ~ 5; 3β, 4 ~ 1.5; 6, 19α ~ 0.5; 6, 7α = 12; 6, 7β = 5; 6, 19α ~ 0.5; 7α, 7β = 14; 7α, 8 ~ 5; 7β, 8 = 2; 11α, 11β = 15; 11α, 12 = 12; 11β, 12 = 1.7; 12, 16 ~ 0.5; 14, 15 = 15, 16 ~ 1.5; 19, 19β = 10; compound **2**: 1, 1′ = 13; 1, 10 = 12; 1′, 10 = 2; 2, 3 = 2; 2′, 3 = 7.5; 6, 7 = 5.5; 11α, 11β = 14; 11α, 12 = 11.5; 11β, 12 = 4; 14, 15 = 15, 16 ~ 1.5; 19α, 19β = 9

occurs in the chair form. The ^{13}C NMR spectral data also agreed with the proposed structure. Compound **1** is related to salviarin (**3**), the configuration of which was determined by X-ray analysis [6]. Here also the A- and the C-ring do not exist in chair conformations. It may be of interest that a clerodane with this stereochemistry has so far not been isolated from the Compositae. But **3** is present in *Tridax peruviensis* Powell (unpublished results).

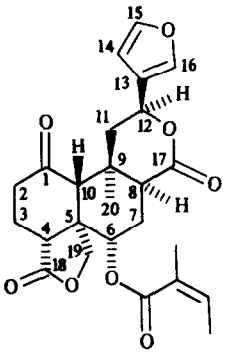
The molecular formula of the second diterpene (**2**) was $C_{20}H_{20}O_6$ and its IR spectrum indicated the presence of a hydroxyl group and a γ-lactone. The ^{1}H NMR spectrum (Table 1) again showed that a β-substituted furan was present. Furthermore, again only one methyl signal was visible (δ0.99 *s*) and a double-doublet at δ5.17 which showed a small coupling with H-16 indicated an oxygen at C-12. Spin decoupling allowed the assignment of all signals leading to sequences which again required the presence of a clerodane derivative which had a 6β-hydroxyl group. The low-field signals at δ7.10 and 6.66 further showed that again two lactone rings were present, but this time both carbonyls were conjugated. The stereochemistry followed from the couplings and from the NOEs between H-20, H-19β and H-11α, while no effect was observed between H-20 and H-12. The $J_{6,7}$ coupling and the downfield shift of H-10 as well as that of H-3 indicated a β-orientation of the hydroxyl group at C-6 on comparison with the chemical shifts of bacchotricuneatin A [7], which only differs from **2** by the missing hydroxyl and the 7,8-double bond.

In the mass spectra of both diterpenes a strong fragment at *m/z* 94 (C_6H_6O) was formed by the splitting of the 12-*O*- and 9,11-bond. This fragmentation is of course favoured in **2**. Accordingly, here *m/z* 94 was the base peak.

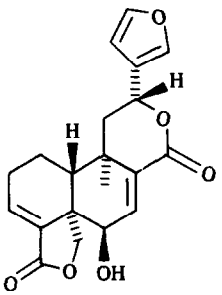
The isolation of **1** and **2** may indicate a relationship between *Aster* and *Baccharis* although this latter genus itself is not very uniform. Further investigations are necessary to see whether similar diterpenes are widespread in the genus *Aster*.

EXPERIMENTAL

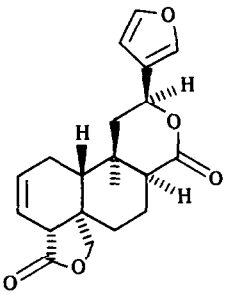
The air-dried aerial parts (50 g, voucher 35/83, collected in the Mongolian Peoples Republic, Chöwsgöl-Aimak, mountain steppes near Buren-Chan, July 1983, voucher deposited at the Institute of Plant Biochemistry (Halle) were extracted with



1



2



3

MeOH–Et_2O–petrol (1:1:1) and the extract was worked up as usual [8]. The CC (SiO_2) fractions were as follows: 1 (petrol and Et_2O–petrol, 1:9), 2 (Et_2O–petrol, 1:3), 3 (Et_2O–petrol, 1:1 and Et_2O) and 4 (Et_2O–MeOH, 9:1). Fractions 1 and 3 gave nothing of interest. TLC (SiO_2 PF 254) of fraction 2 afforded 100 mg dammadienyl acetate and 100 mg dammadienone [both identical with authentic material (^1H NMR, co-TLC and mp)]. TLC of fraction 4 (Et_2O–MeOH, 20:1) gave a mixture (R_f 0.45) which was separated by HPLC (RP 8, MeOH–H_2O, 3:2, 100 bar, flow rate 3 ml/min) affording 10 mg **2** (R_t 2.2 min) and 20 mg **1** (R_t 4.5 min).

6α-Angeloyloxy-1-oxo-2,3-dihydrosalviarin (**1**). Colourless crystals, mp 159–160° ($CHCl_3$–Et_2O); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1740 (δ-lactone), 1720 (C=O, $C=CCO_2R$), 875 (β-furan); MS *m/z* (rel. int.): 456.178 $[M]^+$ (2) (calc. for $C_{25}H_{28}O_8$: 456.178), 374 $[M-O=C=C(Me)CH=CH_2]^+$ (1), 357 $[M-OCOR]^+$ (100), 94 [furanyl-$CH=CH_2$ (A)]$^+$ (28), 83 $[C_4H_7CO]^+$ (73), 55 $[83-CO]^+$ (57);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-18 \quad -19 \quad -22 \quad -48} (CHCl_3;\ c\ 0.1).$$

6β-Hydroxy-7,8-dehydrobacchotricuneatin A (**2**). Colourless crystals, mp 195° (Et_2O); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone), 1740 (δ-lactone), 875 (β-furan); MS *m/z* (rel. int.): 356.126 $[M]^+$ (48) (calc. for $C_{20}H_{20}O_6$: 356.126), 338 $[M-H_2O]^+$ (10), 94 $[C_6H_6O$ (A)$]^+$ (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-90 \quad -95 \quad -108 \quad -189} (CHCl_3;\ c\ 0.27).$$

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