Hydrolysis of **1**. Hydrolysis in 10% HCl at 100° for 2 hr yielded sorbifolin (**2**) mp 290–292°; UV λ_{max}^{MeOH} nm: 253, 308, $AlCl_3$ 263, 323 nm; NaOAc 254, 309 nm. Acetate (Ac_2O–pyridine 24 hr) colourless needles, mp 226–228°. Calc. for $C_{22}H_{18}O_9$; C 61.95, H 4.26. Found; C 62.03, H 4.30%. Methylation of **1** gave a methyl ether (dimethyl sulphate, Me_2CO and K_2CO_3, 24 hr) colourless needles, mp 187–189°. Calc. for $C_{19}H_{18}O_6$; C 66.66, H 5.26. Found; C 66.61, H 5.23%.

Identification of sugar. The sugar fraction from acid hydrolysis of **1** was neutralized in vacuum over NaOH and chromatographed on Whatman No. 1 paper using *n*-BuOH–HOAc–H_2O (4:1:5) and *n*-BuOH–EtOH–H_2O (12:3.3:5.7). Aniline hydrogen phthalate was used as a spraying reagent. Galactose was identified by comparison with an authentic sample.

Scutellarein 7-diglucoside was found identical in all respects to an authentic sample [6].

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FLAVONOID DISTRIBUTION IN *ARNICA* SUBGENUS *CHAMISSONIS*

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Key Word Index—*Arnica*; subgenus *Chamissonis*; Compositae; flavonoids; chemotaxonomy.

Abstract—Twenty-eight flavonoid aglycones have been identified from *Arnica chamissonis*, *A. longifolia*, *A. amplexicaulis*, *A. mollis*, and *A. parryi* of the subgenus *Chamissonis* of the genus *Arnica*. The flavonoid pattern was largely homogeneous. Only *A. mollis* is an exception by the occurrence of 7-methylation.

INTRODUCTION

The genus *Arnica* L. is divided by Maguire [1] into five subgenera and consists of *ca* 32 species, most of which are confined to western North America. As part of a chemosystematic study of *Arnica* we now report on the flavone aglycones in the flowers of five of the seven species of the subgenus *Chamissonis* Maguire. Up to now little was known about the flavonoids of *Arnica* [2–11]. Only subgenus *Austromontana* has been recently intensively examined [12].

RESULTS AND DISCUSSION

Twenty-eight different compounds were isolated and identified by UV, MS and ^{1}H NMR including flavones, flavonols, flavanones and their methyl ethers, some of them with 6-methylation.

Section *Euchamissonis* consists of only one species, *Arnica chamissonis*, which is one of the most widely distributed species of the genus. Maguire differentiates three subspecies: *genuina*, *foliosa* and *incana* [1]. According to the presently accepted nomenclature of Hultén subsp. *incana* is now a variety of *A. foliosa* (see Table 1) [13] and according to Maguire subsp. *chamissonis* represents the stock of subgenus *Chamissonis* [1].

Our chemical examination showed that the flavonoid pattern in section *Euchamissonis* is relatively homogeneous (see Table 1). Besides the ubiquitous compounds **1–4** and the frequently found **5–9**, 11 6-methoxyflavones and -flavonols (**11–21**), which are typical for plants of the Compositae [14] were isolated. However, quercetin 3′,4′-dimethyl ether (**10**) and 6-methoxykaempferol 4′-methyl ether (**17**) are recorded for the first time in the Compositae and patuletin 4′-methyl ether (**20**) for the second time in nature [15]. Patuletin 3′,4′-dimethyl ether (**21**) is a new natural product [11].

Compared with *A. chamissonis* the number of flavonoids in *A. longifolia*, the sole species of section *Eulongifolia*, is reduced and compounds with 4′-methy-

Table 1. Distribution of flavonoid aglycones in *Arnica* subgenus *Chamissonis*

Species	Ap (1)	Lu (2)	Km (3)	Qu (4)	Ap 4'-Me (5)	Lu 3'-Me (6)	Lu 4'-Me (7)	Km 4'-Me (8)	Qu 3'-Me (9)	Qu 3',4'-Me (10)	Ap 6-OMe (11)	Ap 4'-Me, 6-OMe (12)	Lu 6-OMe (13)	Lu 3'-Me, 6-OMe (14)	Lu 3',4'-Me, 6-OMe (15)	Km 6-OMe (16)	Km 4'-Me, 6-OMe (17)	Qu 6-OMe (18)	Qu 3'-Me, 6-OMe (19)	Qu 4'-Me, 6-OMe (20)	Qu 3,4'-Me, 6-OMe (21)	Ap 7,4'-Me (22)	Lu 7,4'-Me (23)	Lu 7,3'-Me (24)	Lu 7,3',4'-Me (25)	Nar 4'-Me (26)	Nar 7,4'-Me (27)	Eri 7,3'-Me (28)
Euchamissonis																												
A. chamissonis																												
subsp. chamissonis	●	●	●	●	●	●		●	○	○	○	○	○	○		○	●	●			○							
var. *interior*																												
subsp. *foliosa*	●	●	●	●	●	●		●	●	○	●	●	●	●	○	●	●	●	●		○				○			
subsp. *foliosa*	○	●	○	●	●		○		○	○	●	●	●	●		○	○		○	○	○							
var. *incana*																												
Eulongifolia																												
A. longifolia	○	●	●	●		○			●		●		●	●				●	●									
Eumollis																												
A. amplexicaulis	○	●	○	●	○	○			○		●	○	●	○		○		●										
A. mollis	○	●	○	●		●					○	○	○	○	○	○	○	●	○		○	○	○	○		○	○	○
A. parryi	●	●	●	●	○	●		○	○		●	●	●	●		●	●	●	○		○	○	○	○		○	○	
subsp. *sonnei*																												

○ = trace, ● = major.

Key: Ap, apigenin; Lu, luteolin; Km, kaempferol; Qu, quercetin; Nar, naringenin; Eri, eriodictyol.

lation are absent. In section *Eumollis*, *A. amplexicaulis* has a smaller number of aglycones than *A. mollis*. *A. mollis* is quite different from other species of this subgenus because of the occurrence of 7-methyl ethers (**22–25**) and flavanones (**27–28**).

According to Maguire *A. parryi* is "probably a recent offshoot of the *A. mollis* stock" [1], but *A. parryi* and *A. chamissonis* subsp. *foliosa*, analysed by us, show the same flavonoid pattern except for compounds **10** and **15**. It differs from that of *A. mollis* by the absence of 7-methylation. Further examinations may show whether the position of *A. parryi* has to be revised. In 1925 Jepson already transferred *A. parryi* subsp. *sonnei* to *A. chamissonis* subsp. *foliosa* (see ref. [1]).

This study shows that in subgenus *Chamissonis* the pattern of flavonoid aglycones is quite homogeneous. Every species examined yields the same skeletal types, the only exception being *A. mollis*. Further work is required to examine the possibility of flavonoid variation in different populations, as found by Wolf and Denford [12], before systematic trends observed can be confirmed with confidence.

EXPERIMENTAL

Plant material. *A. chamissonis* Less. subsp. *chamissonis* Maguire and *A. chamissonis* Less. subsp. *foliosa* (Nutt.) Maguire var. *incana* (Gray) Hultén see ref. [10]. *A. chamissonis* Less. subsp. *foliosa* (Nutt.) Maguire was collected near Mono Lake, California, U.S.A., *A. amplexicaulis* Nutt. was grown from seeds from the Botanical Garden of the University of Vancouver, Canada, *A. mollis* Hooker was grown from seeds from the Botanical Garden of Copenhagen, Denmark and *A. parryi* A. Gray subsp. *sonnei* (Greene) Maguire from seeds from the Botanical Garden of the University of Marburg, West Germany and cultivated in the proving field of the University of Düsseldorf. Flowers were harvested in 1982 and 1983 from June to August. *A. longifolia* D. C. Eaton was cultivated from seeds (origin: Botanical Garden, Wuppertal, West Germany and the Botanical Institute of the Academy of Science, Leningrad, U.S.S.R.) in the proving field of the University of Marburg. Voucher specimens are deposited at the herbarium of the Institute of Pharmaceutical Biology, University of Düsseldorf.

Fractionation and identification. Air-dried powdered flowers of *A. chamissonis* were extracted with MeOH (80%, 50%). The aq. methanolic extracts were concd under red. pres. until only H_2O remained, which was extracted with *n*-hexane, CH_2Cl_2 and EtOAc. Flowers of the other species were extracted with CH_2Cl_2 and subsequently with MeOH. Procedures for the isolation and identification of the compounds from the CH_2Cl_2 extracts have been previously described [10].

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