acids themselves and their methyl esters, compounds 1 and 2 were found to be the *O*-methylated depsidones colensoinic [2] and lobaric acids [3, 4] Exhaustive methylation of compounds 3 and 4 resulted in products with identical IR and MS spectra and identical R_f (TLC) and RR_t (GC) data, the mixed mp was not depressed Their ^{1}H NMR spectra included signals at δ 1 25 (*s*, 24H), 2 70 and 3 12 (*d*, 2CH$_2$, $J = 6\ 5$ Hz), 3 67, 3 71, 3 82 (*s*, 3COOMe), 3 89 (1H, *s* CH) These results suggest that compounds 3 and 4 are caperatic and norcaperatic acids, respectively Compound 5 was identified as fumarprotocetraric acid Norcaperatic acid has not been reported before as a natural lichen component, it had been described as a derivative, obtained while establishing the structure of caperatic acid [5]

Thus, the occurrence of both aliphatic acids and depsidones in *Parmelia stygia* indicates that its chemical composition is much broader than has been noted earlier

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SCOPOLETIN SESQUITERPENE ETHERS FROM *ARTEMISIA PERSICA*[*]

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Abstract—The roots of *Artemisia persica* afforded in addition to isofraxidin-derived sesquiterpene ethers, the scopoletin farnesyl ether scopofarnol and the new scopoletin drimenyl ether scopodrimol A The structures and stereochemistries were elucidated by spectroscopic methods According to the leaf morphology the accumulation of coumarin sesquiterpene ethers also suggests that the species should be transferred from the section *Absinthium* to the section *Abrotanum*

Analysis of sesquiterpene-coumarin ethers in *Artemisia* and *Achillea* is part of a long-range comparative phytochemical investigation within the tribe Anthemideae [1–4] Up to now, 15 derivatives have been isolated from the two genera In contrast to the well-known umbelliferone sesquiterpene ethers mainly isolated from the genus *Ferula* (Umbelliferae) [5], these compounds are uniformly derived from isofraxidin (7-hydroxy-6,8-dimethoxycoumarin) The sesquiterpene moieties have proved to be either open-chain farnesyl or mono- and bicyclic drimenyl derivatives In *Artemisia* they are mainly accumulated in the section *Abrotanum* but have recently also been detected in *Artemisia tripartita* [4] belonging to the North American subgenus *Tridentatae* [6]

During extensive TLC comparisons in UV light, it became apparent that the pale blue isofraxidin-derived sesquiterpene ethers are frequently overlapped by a further set of bright fluorescent blue coumarins which, however, mostly occur only in small amounts Now, from the roots of *Artemisia persica* Boiss (achenes collected near Tashkent, Uzbekistan) sufficient quantities from two components belonging to that series have been isolated for structure elucidation Based on spectral data, the compounds have been shown to be open-chain and bicyclic sesquiterpene ethers linked to scopoletin (7-hydroxy-6-methoxycoumarin) Whereas the scopoletin farnesyl ether (**1**) has already been isolated from *Conyza obscura* [7], the drimenyl ether (**2**) has proved to be new The derivatives were designated as scopofarnol (**1**) and scopodrimol (**2**) Apart from the different coumarinyl moiety, the structures and stereochemistries of the two compounds have been shown to be identical with the isofraxidin-derived farnochrol and drimartol A already isolated from that species [1]

An almost identical composition of coumarin ethers together with scopoletin and isofraxidin has also been established for two further provenances of *A persica* originated from Uzbekistan and Tadshikistan (U S S R)

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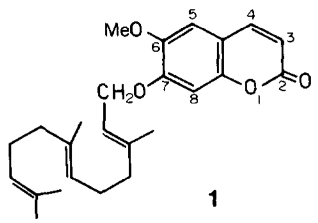
[*] Part 5 in the series "Naturally Occurring Sesquiterpene-Coumarin Ethers" For Part 4 see ref [4]



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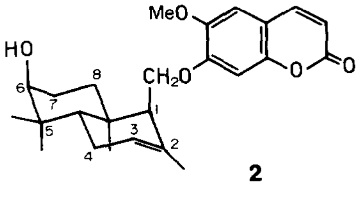

2

Although *A persica* has been considered to be part of the section *Absinthium* because of its hairy receptacles [8], it is obviously more closely related to the section *Abrotanum* on the basis of similar leaf morphology [9] and acetylenic constituents [10] Its affinity with the latter section may also be supported by the distinct accumulation of sesquiterpene-coumarin ethers

The ^{1}H NMR spectra of the scopoletin ethers are characterized by the AB pattern of the protons at C-4 and C-3 (δ7 62 and 6 28, $J = 9$ 5 Hz) and the two remaining aromatic singlets (δ6 83–6 87) [7] In scopofarnol (**1**) the structure of the terpene unit is proved by comparison with the spectrum of farnochrol [1] The chemical shifts of the four methyl groups are in agreement with a *trans-trans*-farnesyl moiety [11, 12] The EI-mass spectrum of **1** clearly deviates from the spectrum of farnochrol Whilst the latter is characterized by fragments derived from the terpenic unit [1], the mass spectrum of **1** shows only one dominant peak at *m/z* 192, which belongs to scopoletin The $[M]^+$ peak is very weak but still observable

The ^{1}H NMR spectrum of scopodrimol A (**2**) shows all characteristic signals for scopoletin ethers All signals of the terpene moiety agree with the *trans*-decalin structure of a drimenol derivative [2, 4] The axial hydroxyl group is proved by the relatively narrow signal for the C-6 proton geminal to the hydroxyl group (δ3 45, $W_{1/2} = 8$ Hz), indicating that this proton is an equatorial one ($W_{1/2}$ for axial C6-H > 15 Hz [1, 4]) The axial position of –CH$_2$O (scop) is clear from the chemical shifts of the corresponding –O–CH$_2$– protons (AB of an ABX system, δ4 28 and 4 02, $\Delta\delta_{A,B} = 0$ 26 ppm) This is typical for axial –CH$_2$OAr moieties in comparable compounds, the corresponding $\Delta\delta$ for equatorial –CH$_2$OAr is generally < 0 1 ppm [1–4] The mass spectrum of **2** shows a small molecular ion peak ($[M]^+$ 2 5%) and a very dominant peak for scopoletin The optical rotation of scopodrimol A (**2**) is $[\alpha]_D$ +160°, which is very close to the umbelliferone and isofraxidin analogues (feropolidin, +155° [5, 13], and drimartol A, +185° [1])

EXPERIMENTAL

The compounds were isolated by a method described previously [1, 4] Air-dried roots (57 g) of *Artemisia persica* (AR-929) afforded 3 mg **1** and 2 mg **2** in addition to the compounds isolated previously [1] Voucher specimens have been deposited at the Herbarium of the Institute of Botany, University of Vienna (WU)

Scopofarnol (**1**), 6-*methoxy*-7-(3,7,11-*trimethyldodeca*-2,6,10-*trienoxy*)-2H-1-*benzopyran*-2-*one* Colourless, viscous oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 2940, 1740, 1560, 1460, 1285, 1150, 1050, 985, UV $\lambda_{max}^{Et_2O}$ nm (ε) 342 (11 500), 295 (6100), 287 (sh, 5500), 258 (sh, 5700), 251 (7400), 228 (20 100), 204 (55 200), MS *m/z* (rel int) (70 eV, 80°) 396 $[M]^+$ (0 5), 193 (43), 192 (100, scopoletin), no other significant peaks with rel int > 10%, ^{1}H NMR see [7]

Scopodrimol A (**2**), (1α,4aα,6α,8aβ)-6-*methoxy*-7[(1,4,4a,5,6,7,8,8a-octahydro-6-*hydroxy*-2,5,5,8a-*tetramethyl*-1-*naphthalenyl*)-*methoxy*]-2H-1-*benzopyran*-2-*one* Colourless crystals from Et$_2$O, mp 155–157°, $[\alpha]_D^{20}$ +160°, $[\alpha]_{436}^{20}$ +410° (*c* 0 25, Me$_2$CO), IR $\nu_{max}^{CCl_4}$ cm^{-1} 3640, 2945, 1740, 1565, 1290, 1150, 1040, 980, UV $\lambda_{max}^{Et_2O}$ nm (ε) 343 (11 300), 295 (6700), 286 (sh, 6000), 258 (sh, 5600), 250 (7300), 227 (20 000), 205 (53 000), MS *m/z* (rel int) (70 eV, 100°) 412 $[M]^+$ (2 5), 193 (39), 192 (100, scopoletin), no other significant peaks with rel int > 10%, ^{1}H NMR (CDCl$_3$) δ7 62 (*d*, 1H, scop C4-H, $J = 9$ 5 Hz), 6 87 and 6 83 (two *s*, 1H each, scop C5-H and C8-H), 6 28 (*d*, 1H, scop C3-H, $J = 9$ 5 Hz), 5 61 (*br m*, 1H, C3-H), 4 28 (*dd*, 1H, C1-CH$_2$O-scop C7, $J_{gem} = 11$ Hz, $J_{vic} = 4$ Hz), 4 02 (*dd*, 1H, C1-CH$_2$O-scop C7, $J_{gem} = 11$ Hz, $J_{vic} = 3$ Hz), 3 88 (*s*, 3H, scop C6-OMe), 3 45 (*br m*, 1H, C6-H, $W_{1/2} = 8$ Hz), 2 20–1 85 (*m*, 5H), 1 80 (*br s*, 3H, C2-Me), 1 75–1 65 (*m*, 3H), 1 20 (*m*, 1H), 1 02 (*s*, 6H, 2Me), 0 96 (*s*, 3H, Me)

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