

Table 1 ESR parameters for vanadium-containing complex compounds

Source	Conditions	g_z	g_{xy}	A_z	A_{xy}
VO(L-ala) ₂	pH 6.6	1.943	1.976	163	55
<i>A. muscaria</i>	*	1.920	1.982	153	45
VO(serine) ₂	pH 11.0	1.955	1.976	150	45
VO(cysteine) ₂	pH 7.8	1.962	1.976	143	45

*Directly measured using a Varian E109 spectrometer on red skin, stipe, gills, volva (and this last repeated after a week was essentially unchanged)

without prior treatment and hence perhaps gain more insight into the mechanism of vanadium metabolism [6]. Similar work on intact plant material may well be feasible with other paramagnetic species like copper(II).

We now wish to report that segments taken from a number of positions from an intact, fresh mushroom all give the same signal (Fig. 1) (although intensities vary due to changes in concentration) and thus show that the same vanadyl complex is present in the red skin, the gills, the

volva and the base. As found previously [3, 4] the highest concentration is obtained in the bulbous base.

Comparisons of the spectra and EPR parameters obtained for segments of the frozen mushroom to those of α -amino acid vanadyl complexes suggest a greater similarity of the chelating ligand to possible terdentate species such as L-cysteine or L-serine rather than to the simpler amino acids such as glycine or L-alanine (Table 1).

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DEPSIDONES AND FATTY ACIDS OF *PARMELIA STYGIA*

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Key Word Index—*Parmelia stygia*, Parmeliaceae, lichen, depsidones, fatty acid, norcaperatic acid.

Abstract—One Russian sample of the lichen *Parmelia stygia* has yielded fumarprotocetraric acid, while a second contained the same compound accompanied by colensoic, lobaric, caperatic and norcaperatic acids.

Parmelia stygia (L.) Ach. is a widespread lichen of alpine zones and highland rocky deserts. Three chemical dissimilar strains of this lichen are known: (a) a fumarprotocetraric acid strain, (b) an acid-deficient strain, and (c) a caperatic acid strain [1]. Strains 'a' and 'b' are generally abundant in arctic regions, while 'c' has only been found so far in Japan and Alaska. We have investigated two samples of *P. stygia*: sample 1 was collected in June 1977 in the Magadan district (lat. 63°N, 600 m on dazite), and sample 2 in July 1981 in the Khabarovsk district (lat. 55°N, 2200 m on rhyolite).

The TLC of an acetone extract of the first sample (3.2% dry wt) showed fumarprotocetraric acid to be the main component; this was identified by direct comparison with an authentic sample. Preparative TLC of an acetone

extract of the second sample (11.4% dry wt) in benzene–acetone (7/3) on silica gel resulted in five components:

- 1—C₂₅H₃₀O₇ (430 mg), mp 173–174°, [M]⁺ 442, methyl ester, mp 54–55°, [M]⁺ 456.
- 2—C₂₅H₂₈O₈ (270 mg), mp 195–197°, [M]⁺ 456, methyl ester, mp 120–121°, [M]⁺ 470.
- 3—C₂₁H₃₈O₇ (423 mg), mp 132–133°, [α]_D²⁰ –24.5° (c 0.2, CHCl₃), IR ν_{\max}^{KBr} 1736, 1687, dimethoxy derivative (diazomethane) mp 55°, [M]⁺ 430.
- 4—C₂₀H₃₆O₇ (152 mg), mp 137–139°, [α]_D²³ –16.0° (c 0.19, EtOH), IR ν_{\max}^{KBr} 1706 (br), trimethyl derivative (diazomethane), mp 55–56°, [M]⁺ 430.
- 5—C₂₂H₁₆O₁₂ (2.6 g), mp 250–260° (dec).

On the basis of IR, ¹H NMR and MS spectral data for the

acids themselves and their methyl esters, compounds 1 and 2 were found to be the *O*-methylated depsidones colensoic [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 , (GC) data, the mixed mp was not depressed. Their ^1H 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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Key Word Index—*Artemisia persica*, Compositae—Anthemideae, sesquiterpene-coumarin ethers

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 coumarin 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 Tadzhikistan (U.S.S.R.)

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