

samples was performed with a LKB-Multiphor apparatus. Gels (0.5 mm thick) containing carrier ampholytes in the pH range 3.5–9.5 were utilized. Samples were applied using filter paper wicks. A constant power of 0.8 W per cm length of gel was passed through the gel at 3° for 2 hr. Gels were prefocused for 30 min. At the end of the experiment, the pink paper was pressed gently onto the gel and the white bands of enzymatic activity were visually discernible in 5–10 min, depending upon the enzymatic activity used. The reaction was interrupted by flooding the gel and paper in 1 mol/l. HCl soln. The paper was removed carefully from the gel and allowed to dry. The gel was fixed and stained with Coomassie Brilliant Blue R-250 for protein detection.

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CHEMICAL VARIATIONS OF *ASAHINEA CHRYSANTHA*

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Key Word Index—*Asahinea chrysantha*; Parmeliaceae; lichen; α - and β -collatolic acids; haematommic acid.

Abstract—A sample of the lichen *Asahinea chrysantha* collected in the northern region of the Soviet Far East contained α - and β -alectoronic acids, while the same lichen collected in the southern region contained the methoxy derivatives, α - and β -collatolic acids, of these two acids.

We recently reported on the chemical composition of a sample of the lichen *Asahinea chrysantha* (Tuck.) Culb. & Culb. collected in the Magadan district (63°N., 1000 m, on granite, sample I) [1, 2].

We have now investigated a sample of the same lichen from the Primorskiy district (44°N., 500 m, on rhyolite, sample II). It had a grey upper surface whereas that of sample I was bright yellow. Other differences of the basic thallus structure could not be found (voucher specimens deposited at the herbarium of the Tartu State University).

The chloroform extract of sample II was chromatographed over Sephadex LH-20 and nine compounds were isolated (see Table 1). Compounds 1, 2, 5–7 and 9–10* were identified by direct comparison with authentic samples (mmp, TLC, MS and NMR). The ninth compound (11) was identical to 1,4,5,6,8-pentahydroxy-3-

methylanthraquinone [MS: m/z 302 $[M]^+$, 286, 274; UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 228, 261, 302; R_f (TLC)]. Its presence in *A. chrysantha* ([1] and this report) and in *A. scholanderi* (Llano) Culb. & Culb. [3] suggests that this pentahydroxymethyl anthraquinone is typical for the genus *Asahinea* and hence we have named it asahinin. There was no possibility of studying the chemical composition of the third species of the genus *Asahinea*, *A. kurodakensis* (Asah.) Culb. & Culb., which contains lavender pigments as well as the other two species [4].

Sample II contained haematommic acid, [MS m/z : 196 $[M]^+$, 178 $[M - H_2O]^+$, 168 $[M - CHO]^+$, 152 $[M - CO_2]^+$; 1H NMR (CDCl₃): δ 2.60 (3H, s, Me), 6.35 (H, s), 10.35 (H, s, CHO), 12.53 (H, s, OH)], a compound that has not been reported before as a natural lichen component [5].

Table 1 shows that sample I contained α - and β -alectoronic acids, while sample II contained the methoxy derivatives of these acids. This is the second report of the

*Structures not shown.

Table 1. Compounds isolated from *A. chrysantha*

No.	Compound	Amount (% dry wt)			Mp
		Molecular formula	Sample I	Sample II	
1	(+)-Usnic acid	C ₁₈ H ₁₆ O ₇	1.39	0.22	202–203°
2	Atranorin	C ₁₉ H ₁₈ O ₅	0.09	0.25	196°
3	α -Alectoronic acid	C ₂₇ H ₃₂ O ₉	0.25	—	192–193°
4	β -Alectoronic acid	C ₂₇ H ₃₂ O ₉	0.31	—	138–139°
5	α -Collatolic acid	C ₂₈ H ₃₄ O ₉	—	0.31	125–126°
6	β -Collatolic acid	C ₂₈ H ₃₄ O ₉	—	0.23	106–108°
7	Methyl β -orcinol-carboxylate	C ₁₀ H ₁₂ O ₄	0.01	0.021	144°
8	Haematommic acid	C ₉ H ₈ O ₅	—	0.003	165–166°
9	Islandicin	C ₁₅ H ₁₀ O ₅	0.001	0.001	217–218°
10	Cynodontin	C ₁₅ H ₁₀ O ₆	0.001	0.001	264°
11	Asahinin	C ₁₅ H ₁₀ O ₇	0.001	0.001	> 320°

presence of β -collatolic acid in the genus *Asahinea* (the first was in the lichen *A. scholanderi* [2]).

These results confirm the prediction by Culberson and Culberson [4] on the chemical variations of *A. chrysantha*.

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