

Dyeing of Wool with Lichens and Lichen Substances

YNGVE JOHANNES SOLBERG

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

Experiments have been carried out in dyeing wool with lichens, lichen substances or their decomposition products and with simple aromatic aldehydes. It is suggested that the formation of azomethine linkages is responsible for the yellow colour obtained under mild dyeing conditions with aldehydic substances. By the usual, more drastic dyeing conditions, where darker colours are developed, the chemical process during dyeing may be more complex.

Some new azomethine compounds with fumarprotocetraric and salazinic acids are described.

I. INTRODUCTION AND GENERAL SURVEY

Dyeing of wool and silk on an industrial scale with lichens has been known in Europe as long as we have records about this craftsmanship, at least as early as the fourteenth century. As a part of domestic industry records may be traced at least 2 000 years further back. The only lichens still used on an industrial scale are giving the well known Orseille dyestuffs. Although the constitution of the pigment is still unknown similar shades may be obtained with other lichens known to contain orcein.

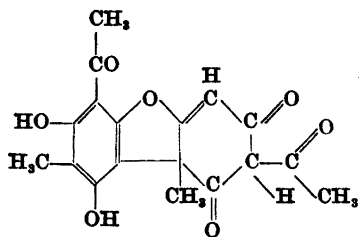
A great number of lichen species which have found use in domestic industry especially for the dyeing of wool does, however, not contain any orcein. By the dyeing procedure mostly used in domestic industry — long boiling of the whole lichens in water followed by introduction of the textiles mostly followed by further boiling — these other lichens give colours ranging from ochre through tawny to a very dull brown.

A broad review of the literature¹⁻¹⁷ revealed that at least 50 different lichen species have been used for dyeing purposes. When the lichens giving Orseille dyes are omitted the 35 species collected in Table 1 remain. In the same table references are given to those of the lichen constituents ("lichen acids") which most reasonably might have some connections with their dyeing properties. Usnic acid (I) one of the most common lichen acids and present in 14 of these lichens is no dyestuff for wool or silk. Most of the aromatic lichen substances are depsides (II) or depsidones (III), compare Table 2.

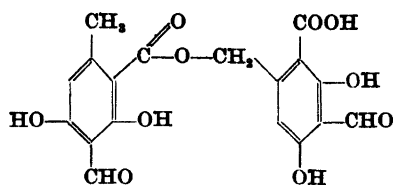
Table 1.

I	II	III	IV
Lichen species	Usnic acid	Depsides or depsidones of aldehydic structure	Other lichen acids
<i>Parmelia centrifuga</i>	1	2	16
» <i>saxatilis</i>		2	8
» <i>conspersa</i>	1	2	7
» <i>olivacea</i>		5 6	
» <i>sulcata</i>		2	8
» <i>physodes</i>		2	6b
» <i>omphalodes</i>		2	8
» <i>pertusa</i>		2	7
» <i>encausta</i>		2	5 6
» <i>furfuracea</i>		2	
» <i>stenophylla</i>	1	2	8
» <i>acetabulum</i>		2	7b
» <i>stygia</i>		2	5 6
<i>Cetraria islandica</i>		5	19, 20
» <i>glauca</i>		2	21
<i>Ramalina siliquosa</i>	1		7
» <i>farinacea</i>	1		6
» <i>subfarinacea</i>	1		8
» <i>calicaris</i>	1		10, 14
» <i>cuspidata</i>			11
<i>Usnea barbata</i>	1	3	
» <i>florida</i>	1	4	
» <i>hirta</i>	1	4	
» <i>plicata</i>	1		8
<i>Baeomyces placophyllus</i>			7
<i>Stereocaulon coralloides</i>		2	7
<i>Cladonia rangiferina</i>		2	5
» <i>pyxidata</i>			5
<i>Lobaria pulmonaria</i>			7
<i>Evernia prunastri</i>	1	2	13, 14
» <i>vulpina</i>		2	23
<i>Alectoria cana</i>		2	8 9
<i>Haematomma ventosum</i>	1		15
» <i>coccineum</i>	1	2	22, one fatty acid
» <i>leiphaemum</i>		2	one fatty acid

1) Usnic acid, 2) Atranorin, 3) Barbatolic acid, 4) Thamnic acid, 5) Fumarprotocetraric acid, 6) Protocetraric acid, 6b) Mono-acetylprotocetraric acid, 7) Stictic acid, 7b) Norstictic acid, 8) Salazinic acid, 9) Psoromic acid, 10) Obtusatic acid, 11) Cuspidatic acid, 12) Sekikaic acid, 13) Barbatic acid, 14) Evernic acid, 15) Divaricatic acid, 16) Alectoronic acid, 17) Physodic acid, 18) Lobaric acid, 19) Protolichesterinic acid, 20) Lichesterinic acid, 21) Caperatic acid, 22) Hymenorhodin, 23) Vulpinic acid.

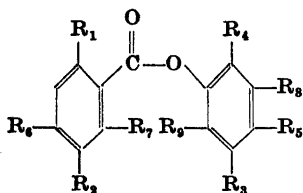


I Usnic acid

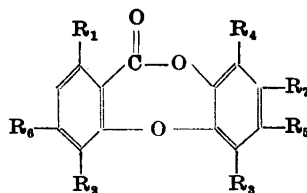


VI Barbatolic acid

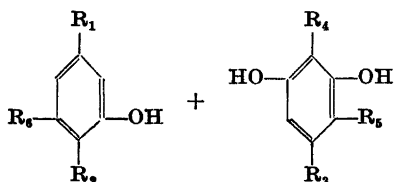
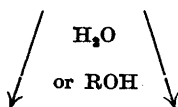
Inspection of Tables 1 and 2 reveals that most of the non-Orseille lichens used for the dyeing of wool contain aromatic compounds with at least one-aldehyde function. Of the 12 lichen acids with an aldehyde function in Table 2, four have been tested as pure substances for their dyestuff properties. It turned out that if these aldehydic depsides or depsidones were applied in aqueous acetone or 90 % alcohol at room temperature, the wool took on a bright yellow to yellowish brown colour, whereas boiling under reflux for 2 hours produced the much stronger reddish to brown colours which are usually obtained when dyeing with lichens. In the 2nd chapter is demonstrated that aldehydic depsides or depsidones with different amines give azomethine compounds of yellow to orange colours. Thus it seems probable that the bright colours developed on wool from solutions in organic solvents may be azo-



II Depsides



III Depsidones



IV

V

Table 2.

Reference number, Table 1	Depside lichen acids	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	R ₉	
2	Atranorin	CH ₃	CHO	CH ₃	CH ₃	COOCH ₂ CCH ₃	OH	OH	OH	H	
4	Thamnolic acid	CH ₃	COOH	CHO	CH ₃	OH	OCH ₃	OH	COOH	OH	
10	Obtusatic acid	CH ₃	CH ₃	CH ₃	H	COOH	OCH ₃	OH	OH	H	
12	Sekikaic acid	C ₃ H ₇	H	H	OH	C ₃ H ₇	OCH ₃	OH	COOH	OCH ₃	
13	Barbatic acid	CH ₃	CH ₃	CH ₃	CH ₃	COOH	OCH ₃	OH	OH	H	
14	Evernic acid	CH ₃	H	CH ₃	H	COOH	OCH ₃	OH	OH	H	
15	Divaricatic acid	C ₃ H ₇	H	C ₃ H ₇	H	COOH	OCH ₃	OH	OH	H	
	Depsidone lichen acids										
5	Fumarprotocetraric acid	CH ₃	CHO	CH ₃	CH ₂ O.CO.CH CH.COOH	COOH	OH	OH	OH	OH	
6	Protocetraric acid	CH ₃	CHO	CH ₃	CH ₂ OH	COOH	OH	OH	OH	OH	
6b	Mono-acetylprotocetraric acid	CH ₃	CHO	CH ₃	CH ₂ O.CO.CH ₃	COOH	OH	OH	OH	OH	
7	Stictic acid	CH ₃	CHO	CHO	CH ₃	COOH	OCH ₃	OH	OH	OH	
7b	Norstictic acid	CH ₃	CHO	CHO	CH ₃	COOH	OH	OH	OH	OH	
8	Salazinic acid	CH ₃	CHO	CHO	CH ₂ OH	COOH	OH	OH	OH	OH	
9	Psoromic acid	CH ₃	CHO	COOH	CH ₃	H	OH	OCH ₃	OH	OH	
16	Alcetriconic acid	CH ₃ .CO.H ₁₁ C ₆	H	CH ₂ .CO.H ₁₁ C ₆	H	COOH	OH	OH	OH	OH	
17	Physodic acid	CH ₃ .CO.H ₁₁ C ₆	H	C ₆ H ₁₁	H	COOH	OH	OH	OH	OH	
18	Lobaric acid	CO.C ₄ H ₉	H	C ₃ H ₁₁	H	COOH	OCH ₃	OH	OH	OH	

methine compounds formed from the aldehydic function of the lichen acids and free amino residues in the wool.

A confirmation of this hypothesis follows from the fact that evernic acid (14, see Table 2) and lobaric acid (18, see Table 2) which do not contain any aldehydic group give no colour on wool. We suppose that the closely related depsides obtusatic acid (10), barbatic acid (13), divaricatic acid (15) and the depsidones alectoronic acid (16) and physodic acid (17) will prove to be without dyeing properties.

That hydroxyaldehydes take part in the dyestuff formation was demonstrated with simple aromatic compounds. Methanolic solutions of salicylic aldehyde, 2,4-dihydroxy-benzaldehyde, 4,6-dimethyl-2-hydroxybenzaldehyde and vanillin all gave strong colours on wool. Piperonal and cinnamic aldehyde, however, also developed yellow colours on wool demonstrating that free hydroxygroups may be absent.

It is well known that lichen depsides are hydrolysed by boiling water $\text{II} \rightarrow \text{IV} + \text{V}$ (Refs.^{18, 19}). From atranorin (2) atranol (IV: $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{CHO}$, $\text{R}_6 = \text{OH}$) and β -orcinol carboxylic acid methyl ester (V: $\text{R}_3 = \text{R}_4 = \text{CH}_3$, $\text{R}_5 = \text{COOCH}_3$) were prepared. The orcinol carboxylic acid methyl ester did not dye wool; atranol refluxed with water and wool gave the same colour as did atranorin (2). The strong tawny colours produced during the process used in domestic industry, could then be due not to the aldehydic lichen acids themselves, but to their decomposition products generated by hydrolysis.

The chemistry of the dyeing process is obviously more complicated in the case of a native lichen than when using the corresponding lichen substances. Experience has really shown that the colour obtained with native lichen is deeper and richer than the colour which results from treatment with the isolated lichen substances. We know to-day that the aldehydic lichen substances are present in a very great number of lichen species (atranorin or chloroatranorin has been demonstrated in more than eighty different species), and that lichens which contain one or more of them always give colour with wool.

In Table 1 *Ramalina calicaris* figures as a dye lichen. This lichen is known to contain usnic (1), evernic (14) and obtusatic acid (10), none of which contains an aldehyde group. As mentioned above usnic acid does not act as a dyestuff. Pure evernic acid (from *Evernia prunastri*) was tested and as expected was found to be negative. Since obtusatic acid is the methyl homologue of evernic acid also this lichen acid most likely is not colour-forming. Since literature gives no informations about the colour obtained with *Ramalina calicaris* dyeing experiments were carried out with the whole lichen. The wool took on a green colour. The dyeing properties of *Ramalina calicaris* thus is due to quite another type of dyestuff formation.

The dye lichens *Ramalina cuspidata* and *Haematomma ventosum* are also said to be free from aldehydic substances. Lack of material has prevented examination of these lichens.

II. NEW AZOMETHINE COMPOUNDS WITH FUMARPROTOCETRARIC ACID AND SALAZINIC ACID

It appears that comparatively few azomethine compounds of depsidone aldehydes and derivatives have been studied²⁰⁻²⁶. Aniline, bromoaniline, phenylhydrazine and *p*-nitrophenylhydrazine have been used as amino components. These azomethine compounds are yellow substances, easily decomposed into their components by treatment with diluted hydrochloric or sulphuric acid. Most frequently they are slightly soluble in the common organic solvents.

The synthesis of five new azomethine compounds is reported in this paper: *p*-aminobenzoic acid-*N*-fumarprotocetraric acid, glycine methyl ester-*N*-fumarprotocetraric acid, methyl anthranilate-*N*-fumarprotocetraric acid, methyl *m*-aminobenzoate-*N*-fumarprotocetraric acid and di(methyl *m*-aminobenzoate-*N*-)salazinic acid.

The yellow colour of these azomethine compounds resembles closely the colour obtained when wool is dyed under certain conditions with fumarprotocetraric acid, atranorin, chloroatranol and simpler aromatic aldehydes. This seems to support the suggestion put forward above that azomethine linkages are formed when fibres of wool and silk react with aromatic aldehydes. The fact, however, that the dyeing under other conditions will give darker colours (tawny, brown, redbrown) would indicate that the chemical process in such cases is more complex.

The azomethine compounds described in the experimental part are hygroscopic substances, amorphous or crystalline. They have no definite melting point, but decompose above two hundred degrees.

EXPERIMENTAL

Isolation of lichen substances

The following aldehyde depsidones have been isolated: Fumarprotocetraric acid from *Cetraria islandica* and salazinic acid from *Parmelia saxatilis*. The isolation of the depsidones was carried out mainly according to the methods described by Simon, Hesse, Zopf, Koller, Klein, Pöpl and Asahina^{2, 15, 20-23, 27-31}.

Preparation of azomethine compounds

I. *p*-Aminobenzoic acid-*N*-fumarprotocetraric acid. To 2 g of fumarprotocetraric acid, dissolved in the minimum amount of pyridine, was added an ethanolic solution of 0.6 g of *p*-aminobenzoic acid. The mixture immediately turned dark yellow. On dilution with 80 ml hot ethanol and standing, microscopic, yellow needles were precipitated. The condensation product was purified by recrystallization from acetone-petroleum ether (1:2). Yield: 1.3 g. (Found: C 58.6; H 4.3; N 2.2; equiv.wt. 145.4. Calc. for C₂₉H₂₁O₁₃N: C 58.9 H 3.6; N 2.4; equiv.wt. 147.9.)

The substance was easily soluble in cold pyridine and dioxan, soluble in hot acetone and ethanol, insoluble in ether, ethyl acetate, xylene, chloroform and benzene. An ethanolic solution of the compound gave an intensely red colour with *p*-phenylenediamine. The yellow colour of the condensation product disappeared on treatment with diluted hydrochloric acid, indicating that the compound was decomposed. In diluted alkali the compound was stable for some time (5-7 min.).

II. *Glycine methyl ester-N-fumarprotocetraric acid*. Fumarprotocetraric acid (1 g), glycine methyl ester (0.5 g), dry methanol (50 ml) and dry acetone (50 ml) were shaken in a bottle at room temperature for 15 h. By evaporation of the solvents a yellow, amorphous product was precipitated. The condensation product was purified by washing with much petroleum ether and then dried at 80° for 15 h. (Found: C 55.7; H 4.4; N 2.5; CH₂O 5.8. Calc. for C₂₅H₂₁O₁₃N: C 55.3; H 3.9; N 2.6; CH₂O 5.7.) The condensation product was found to be easily soluble in ethanol and acetone, slightly soluble in ether, petroleum ether and benzene.

III. *Methyl anthranilate-N-fumarprotocetraric acid*. Fumarprotocetraric acid (1 g), methyl anthranilate (0.5 g), acetone (75 ml) and 96 % ethanol (75 ml) were shaken at room temperature for 15 hours. After filtration the solution was evaporated to dryness. The yellow residue was purified by treatment with petroleum ether. Before analysis the azomethine compound was dried at 60° for 15 h. (Found: C 59.4; H 4.2; N 2.4. Calc. for C₃₀H₂₃O₁₃N: C 59.5; H 3.8; N 2.3). The substance was soluble in acetone and ethanol, insoluble in petroleum ether and benzene.

IV. *Methyl m-aminobenzoate-N-fumarprotocetraric acid*. This azomethine compound was prepared in two different ways.

a) Fumarprotocetraric acid (1 g) and methyl *m*-aminobenzoate (0.7 g) were shaken with a mixture of 100 ml dry acetone and 100 ml absolute ethanol at room temperature. Yellow, transparent needles precipitated gradually. After 24 h the condensation product was filtered and treated with 75 ml ether for 20 h. Next dried at 100°. (Found: C 59.9; H 4.2; N 2.3; CH₂O 5.1. Calc. for C₂₅H₂₃O₁₃N: C 59.5; H 3.8; N 2.3; CH₂O 5.1.) The azomethine compound was insoluble in ether, benzene and petroleum ether, slightly soluble in acetone and ethanol, easily soluble in warm glycol monoethyl ether.

b) Fumarprotocetraric acid (1.5 g) was dissolved in 700 ml hot 80 % acetone. To this solution methyl *m*-aminobenzoate (1 g), dissolved in 150 ml 96 % ethanol, was added. The mixture immediately turned dark yellow. By evaporation of the solvents a yellow, amorphous product was precipitated. The condensation product was purified by shaking it with 50 ml ethanol for 20 h. (Found: C 60.1; H 4.2; N 2.2; CH₂O 5.6. Calc. for C₃₀H₂₃O₁₃N: C 59.5; H 3.8; N 2.3; CH₂O 5.1.)

V. *Di(methyl m-aminobenzoate-N-)salazinic acid*. Salazinic acid (2.5 g) was dissolved in 600 ml boiling 80 % acetone. Methyl *m*-aminobenzoate (4 g) dissolved in 50 ml acetone was added. The deep yellow solution was filtered and diluted with 1.2 liter cold water. Hereby the condensation product was precipitated. It was purified by recrystallization from acetone-water (1:2). Yield 2.5 g. (Found: C 62.0; H 4.3; N 4.1; CH₂O 9.5. Calc. for C₂₄H₂₀O₁₃N₂: C 62.4; H 4.0; N 4.3; CH₂O 9.5). This azomethine compound was easily soluble in hot acetone, slightly soluble in ethanol and insoluble in ether and benzene. An ethanolic solution gave a brown-violet colour with ferric chloride. In conc. sulphuric acid the azomethine compound dissolved with a red colour.

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Received January 15, 1956.