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# Short Communications

## Studies on the Chemistry of Lichens

## IX.* On the Identity of Ocellatic acid and Thamnolic acid

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The lichen *Pertusaria corallina* (Ach) was investigated by Hesse [1] who isolated from it a phenolic acid of low solubility called ocellatic acid, m. p. 208° (decomp.) which analysed for $C_{21}H_{18}O_{12}$ and contained a methoxyl group. An acid, evidently identical with ocellatic acid has now been isolated from *P. corallina* which grows abundantly in the vicinity of Stockholm. The substance was conveniently crystallised from dioxan and after drying analysed for $C_{19}H_{16}O_{11}$. This formula agrees with that of thamnolic acid, m. p. 223° (decomp.), isolated by Zopf from *Thamnolia vermicularis* (Sw.) Ach. and investigated in detail by Asahina *et al.* who found it to be a depside of structure I (for references see[2]). The only known derivative of thamnolic acid melting without decomposition is the dimethyl ester (m. p. 158°) obtained in small yields by Asahina *et al.* through cautious methylation with diazomethane. When methylated according to Asahina, ocellatic acid gave a dimethyl ester of m. p. 157—158°.

For direct comparison thamnolic acid was isolated from *Thamnolia vermicularis*. It crystallised with one molecule of dioxan, melted at 210—212° (decomp.) and gave the same colour reactions as ocellatic acid. The two substances also proved identical on paper chromatography [3]. A full proof of their identity was obtained by comparing their infra-red spectra in the region 5—10 $\mu$ where both acids gave the same characteristic bands.

The identity of ocellatic and thamnolic acid gives further proof to the wide distribution in lichens of the latter, formerly believed to occur only in *Thamnolia* and in members of the family *Cladoniae*. The occurrence of thamnolic acid in another *Pertusaria* species, *P. dealbeata* Nyl., was recorded by Koller and Hamburg [4].

*Experimental* *. *Ocellatic acid.* *P. corallina* (160 g) was extracted with ether in a Soxhlet-apparatus for several days yielding 4.5 g of a crude acid which proved to be homogeneous on paper chromatography [3]. $R_F = 0.06$ on paper impregnated with 0.1 M $Na_2HPO_4$ (*n*-butanol-water) and $R_F = 0.15$ on unimpregnated paper (*n*-butanol-ethanol-water 4:1:5). The chromatograms were observed in ultra-violet light (greenish white spots) and sprayed with a solution of *p*-phenylenediamine (yellow spots) or *bis*-diazotised benzidine (red spots).

For analysis the acid was crystallised several times from dioxan yielding prisms of a faintly yellowish colour containing dioxan of crystallisation, completely lost only after drying *in vacuo* at 100°; m. p. 221—223° (decomp.). Loss of weight, found: 16.8 %. $C_{19}H_{16}O_{11}$, $C_4H_8O_2$, requires 17.3 % dioxan. Found: C 54.3; H 3.91; $OCH_3$ 7.36. $C_{19}H_{16}O_{11}$ requires C 54.3; H 3.82; $OCH_3$ 7.37.

The dimethyl ester was prepared according to Asahina *et al*[5]. by adding the calculated amount of ethereal diazomethane to a supersaturated solution of the acid (170 mg) in acetone (500 ml) at —15°. Prisms (30 mg) from benzene-ethanol, m. p. 157—158°. Found: $OCH_3$, 20.4. $C_{21}H_{20}O_{11}$ requires $(OCH_3)_3$ 20.8.

*Thamnolic acid.* *Thamnolia vermicularis (sensu* Asahina) which is known to contain only thamnolic acid was picked out by its dark blue colour under the ultra-violet light from a mixture with *Thamnolia subvermicularis*

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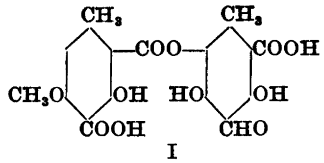
* All melting points uncorrected.



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(Asahina) which contains squamatic and baeomycessic acids and which shows a quite distinct bright white fluorescence. By extracting the pure lichen (10 g) with ether in a Soxhlet-apparatus, crude thamnolic acid (1 g) was obtained. It was chromatographically indistinguishable from ocellatic acid and was obtained from dioxan as prisms containing one mole of dioxan, lost after drying *in vacuo* at 100°. Found: Loss of weight: 17.0 %. $C_{19}H_{16}O_{11},C_4H_8O_2$ requires 17.3 % dioxan. Found: Equiv.wt. 205. $C_{19}H_{16}O_{11}$ requires equiv.wt. 210.1.

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1. Hesse, O. *J. prakt. Chem.* **63** (1901) 551.
2. Asahina, Y. and Shibata, S. *Chemistry of lichen substances*, Tokyo 1954.
3. Wachtmeister, C. A. *Acta Chem. Scand.* **6** (1952) 818.
4. Koller, G. and Hamburg, H. *Monatsh.* **65** (1935) 375.
5. Asahina, Y. Aoki, M. and Fuzikawa, F. *Ber.* **74** (1941) 828.

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## The Standard Oxidation Potential of the System, 1,4-Naphthoquinone/H+ — 1,4-Naphthohydroquinone and the Solubility of 1,4-Naphthohydroquinone, 1,4-Naphthoquinone and 1,4-Naphthoquinhydrone

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Previously LaMer and Baker have determined by electrometric titration the standard oxidation potential of the system 1,4-naphthohydroquinone = 1,4-naphthoquinone + $2H^+$ + 2e at 25° C. They found the value 0.4698 ± 0.0002 volt [1]. Many other values are reported in the literature, but they have all been determined in non-aqueous solutions, and are therefore incomparable to the value here reported.

The solubility of 1,4-naphthohydroquinone, 1,4-naphthoquinone and 1,4-naphthoquinhydrone has not been determined before. The solubilities of 1,4-naphthoquinone and 1,4-naphthohydroquinone presented in this paper have been determined directly, that of 1,4-naphthoquinhydrone has been calculated as shown below.

The standard oxidation potential presented in this paper for the system in question at 20° C in an aqueous solution of 0.01 M HCl + 0.09 M KCl was determined in two ways (see Table 1) combined with the determination of the solubility of 1,4-naphthoquinone and of 1,4-naphthohydroquinone.

Denoting the electromotive forces of the three cells by $E_A$, $E_B$ and $E_C$, respectively we have the following equations: (the liquid-liquid junction potential being taken as zero)

$\pi_0' - E_A = \pi_0$, $\pi_0' - E_B = \pi_B$ and $\pi_0' - E_C = \pi_C$, where $\pi_0'$ and $\pi_0$ are the standard oxidation potentials of the systems benzoquinone—benzohydroquinone and 1,4-naphthoquinone — 1,4-naphthohydroquinone, respectively; $\pi_B$ and $\pi_C$ are the oxidation potentials at pH = 0 in the left half-cells of (B) and (C). $\pi_0$ and the solubility product of 1,4-naphthoquinhydrone $L$ may be calculated from $\pi_B$, $\pi_C$ and the solubilities of 1,4-naphthoquinone ($c_{oQu}$) and 1,4-naphthohydroquinone ($c_{oHy}$):

$$\pi_B = \pi_0 + 0.02905 \log c_{oQu}/c_{Hy} \text{ and}$$
$$\pi_C = \pi_0 + 0.02905 \log c_{Qu}/c_{oHy} \text{ and}$$
$$c_{Qu}c_{oHy} = c_{oQu}c_{Hy} = L$$

$c_{Hy}$ and $c_{Qu}$ are the concentrations of 1,4-naphthohydroquinone and 1,4-naphthoquinone in the left half-cells of (B) and (C), respectively. The following results were obtained: ($\pi_0'$ is taken as 0.7028 volt [2]) $c_{oQu} = (1.099 \pm 0.005)\ 10^{-3}$ mole/liter, $c_{oHy} = (5.25 \pm 0.03)\ 10^{-3}$ mole/liter. $E_A = 0.2211 \pm 0.0005$ volt, $E_B = 0.2092 \pm 0.0001$ volt, $E_C = 0.2735 \pm 0.0001$ volt. The value of $\pi_0$ calculated by means of $\pi_0'$ and $E_A$ is 0.4817 ± 0.0005 volt. The value of $\pi_0$ calculated by means of $\pi_0'$, $E_B$, $E_C$, $c_{oQu}$, and $c_{oHy}$ is 0.4812 ± 0.0002 volt. The calculated value for $L$ and the solubility of 1,4-naphthoquinhydrone are