Short Communications

Studies on the Chemistry of Lichens
IX.* On the Identity of Ocellatic acid and Thamnolic acid
CARL AXEL WACHTMEISTER
Institutionen för organisk kemik, Kungl.
Tekniska Högskolan, Stockholm, Sweden

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 \(C_{11}H_{14}O_6\) and contained a methoxy 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 \(C_{11}H_{14}O_6\). 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 deposite of structure I (for references see\(^6\)). 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\(^5\). 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 Cladoniaceae. The occurrence of thamnolic acid in another Pertusaria species, \(P. \) dealbatae 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 4.6 g of a crude acid which proved to be homogeneous on paper chromatography\(^5\). \(R_F = 0.06\) on paper impregnated with \(0.1 \text{ M Na}_2\text{HPO}_4\) (n-butanol-water) and \(R_F = 0.15\) on unimpregnated paper (n-butanol-ethanol-water 4:1:5). The chromatograms were observed in ultraviolet 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: 18.8 %. \(C_{11}H_{14}O_11\), \(C_{11}H_{22}O_6\), requires 17.3 % dioxan. Found: C 54.3; H 3.91; OCH\(_3\) 7.35. \(C_{11}H_{14}O_{12}\) requires C 54.3; H 3.82; OCH\(_3\) 7.37.

The dimethyl ester was prepared according to Asahina et al.\(^6\), 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. \(C_{11}H_{22}O_{11}\) requires (OCH\(_3\)) 20.8.

Thamnolic acid. Thamnolia vermicularis (sensus 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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The Standard Oxidation Potential of the System, 1,4-Naphthoquinone/H+ — 1,4-Naphthohydroquinone and the Solubility of 1,4-Naphthoquinone, 1,4-Naphthoquinone and 1,4-Naphthoquinhydron

ULRIK KLING

Universitetsfysikal-kemiakte institut,
Copenhagen, Denmark

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. 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-naphthoquinhydron 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-naphthoquinhydron 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 I) 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)

$$
p_s' - E_A = p_s, \quad p_s' - E_B = p_B, \quad p_s' - E_C = p_C,
$$

where $p_s'$ and $p_s$ are the standard oxidation potentials of the systems benzoquinone—benzohydroquinone and 1,4-naphthoquinone — 1,4-naphthohydroquinone, respectively; $p_B$ and $p_C$ are the oxidation potentials at pH = 0 in the left half-cells of (B) and (C). $p_s$ and the solubility product of 1,4-naphthoquinhydron $L$ may be calculated from $p_B$, $p_C$ and the solubilities of 1,4-naphthoquinone ($c_{QA}$) and 1,4-naphthohydroquinone ($c_{HY}$):

$$
p_B = p_s + 0.05905 \log c_{QA}/c_{HY} \quad \text{and} \quad p_C = p_s + 0.05905 \log c_{QA}/c_{HY} \quad \text{and} \quad c_{QA}/c_{HY} = c_{QA}/c_{HY} = L
$$

cHY and cQA 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: ($p_s'$ is taken as 0.7028 volt) $c_{QA} = (1.099 ± 0.005) \times 10^{-9}$ mole/liter, $c_{HY} = (6.25 ± 0.03) \times 10^{-4}$ mole/liter, $E_A = 0.2211 ± 0.0005$ volt, $E_B = 0.3092 ± 0.0001$ volt, $E_C = 0.2735 ± 0.0001$ volt. The value of $p_s$ calculated by means of $p_s'$ and $E_A$ is 0.4817 ± 0.0005 volt. The value of $p_s$ calculated by means of $p_s'$, $E_B$, $E_C$, $c_{QA}$, and $c_{HY}$ is 0.4812 ± 0.0002 volt. The calculated value for $L$ and the solubility of 1,4-naphthoquinhydron are

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