Short Communications

Infrared Absorption Spectra of Aluminium Soaps of Rosin Acids

HENRIK H. BRUUN

Department of Medical Biochemistry, Institute of Medical Chemistry, University of Uppsala, Sweden; Institute of Physical Chemistry, Åbo Akademi, Finland

Harple, Wiberley and Bauer ¹ have studied the infrared spectra of aluminium soaps of fatty acids synthesized by an aqueous metathesis method. They found that both aluminium soaps with one mole of aluminium to two moles of fatty acid (disoap) and those with one mole of aluminium to one mole of fatty acid (monosoap) exist as distinct chemical compounds. They were unable, however, to establish the existence of a trisoap. The spectra of the disoaps contained a free hydroxyl band (2.7 μ), those of the monosoaps a band of bonded hydroxyl (3.0 μ).

The present paper gives the results of an infrared spectroscopic study of the structure of aluminium soaps of rosin acids. The substances investigated were the aluminium monoscaps of tetrahydroabietic and isodextropimaric acids and five samples of the former acid containing different amounts of aluminium from the nearly pure acid to the monoscap. For comparison, aluminium monomyristate was also investigated.

Experimental. Monolayer studies of various rosin acids ², purified tall oil rosin acid (a mixture of rosin acids) ³⁻⁵ and myristic acid ⁶⁻² have shown that these acids react with aluminium ions under suitable conditions when they are spread in a monomolecular layer on the surface of an aluminium salt solution. At certain pH values and aluminium concentrations aluminium soaps are produced in which

the molar ratio of aluminium to acid is unity or less than unity. (The compositions of the monolayers were determined on the dried monolayer substances after they had been skimmed from the substrate surface.) samples studied in this investigation were prepared on the basis of this experience. The substrates from which the monolayer substances were collected by skimming were 0.001 M in potassium aluminium sulphate; in the preparation of the monoscaps the pH was 4.30 and in the preparation of the five samples of tetrahydroabietic acid containing different amounts of aluminium the pH's were 3.70, 3.84, 4.00, 4.12 and 4.24. The compositions of the samples were checked by micro combustion analyses *, which gave a carbon content of 67.2 wt % for the monoscap of the tetrahydroabietic acid (calculated carbon content of dibasic aluminium monosoap, 66.3 %, of monobasic aluminium disoap, 74.3 %, and of aluminium trisoap, 77.3 %) and carbon contents 77.8, 76.2, 73.9, 71.6 and 69.1 % for the five samples (calculated carbon content of pure tetrahydroabietic acid, 78.3 %). samples on which the analyses and spectroscopic studies were made were previously dried at 80-90°C in a vacuum over phosphorus pentoxide.

The infrared absorption spectra were recorded with a double beam spectrophotometer ** of the type described by Hornig, Hyde and Adcock¹0. The samples were prepared for the measurements by the potassium bromide technique.

Results and conclusions. The infrared absorption spectra of the aluminium monoscaps of the tetrahydroabietic and isodextropimaric acids showed the following strong (s) and medium (m) absorption bands (in μ): 3.0 (m), 3.4-3.5 (s), 5.9 (m), 6.3 (s), 6.8-6.9 (s), 6.9-7 (s), 7.2 (m), 7.3 (m), 10.0-10.2 (s), 11.0 (s) (only for

^{*} These analyses were performed in the Microanalytical Laboratory of the Institute of Medical Chemistry of Uppsala University.

** Built by Dr. M. Skog.

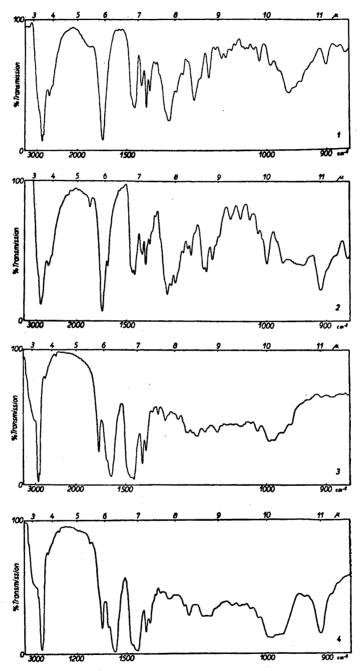


Fig. 1. Infrared absorbtion spectra of 1) tetrahydroabietic acid, 2) isodextropimaric acid, 3) aluminium monoscap of tetrahydroabietic acid, 4) aluminium monoscap of isodextropimaric acid.

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the monoscap of isodextropimaric acid), 12.9-13.0 (m). The bands at 3.4-3.5. 6.8-6.9, 7.2 and 7.3 μ are due to the hydrocarbon part of the rosin acid molecule (these bands appear also in the spectra of the pure rosin acids), that at 3.0μ to associated hydroxyl groups, the bands at 6.3, 6.9-7 and $10.0-10.2 \mu$ to the carboxylate group of the aluminium soap. With the exception of the band 5.9 μ , which is due to the presence of small amount of unreacted acid in the sample (the unreacted acid gives weak absorption bands also at other wave lengths) and the band at $12.9-13.0 \mu$, the spectra are in good agreement with that for aluminium monomyristate and those of the aluminium monosoaps of a-ethylcaproic and lauric acids recorded by Harple, Wiberley and Bauer 1. From these results it may be concluded that the aluminium monosoaps of the rosin acids exist as definite chemical Other evidence favouring compounds. this conclusion has already been presented earlier 3, 9, 5.

The spectra of the samples of tetrahydroabietic acid containing different amounts of aluminium exhibited the following changes with increasing aluminium content. The band at 3.0 μ appears while at the same time the band for dimeric carbocylic acid $(3.8-4 \mu)$ becomes weaker. The very strong band of the C=O vibration absorption (5.9 μ) is suppressed to a small peak. Bonds at 6.3 and $6.9-7 \mu$ due to carboxylate groups appear already at a very low aluminium content (in the sample collected at pH 3.84). The bands at 7.1, 7.8, and 10.5 μ typical of carboxylic acids are greatly reduced in intensity. None of the recorded spectra revealed an absorption band at 2.7μ characteristic of an aluminium discap. It thus appears that no aluminium discap of the type found with fatty acids is formed. The samples of tetrahydroabietic acid containing less aluminium than the amount corresponding to a monosoap involves a system composed of only two components, the aluminium monoscap and rosin acid. This conclusion is confirmed by the observed absorption due to the free acid in the spectra of the samples of high aluminium content *.

The band at $10.0-10.2~\mu$ is assumed to be due to the Al-O linkage, the band is found also in the spectra of the different aluminium scaps of the fatty acids investigated by Harple, Wiberley and Bauer 1.

A detailed report of this investigation will be published later.

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^{*} Back and Steenberg * have isolated a compound corresponding to aluminium discap from dried aluminium soap precipitates of abietic acid by extraction with anhydrous scetone.