329. *Lichen Acids. Part VI. Constituents of* Ramalina scopulorum.

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FROM *Ramalina scopulorum* grown on the coast of Sweden, Zöpf (*Annalen*, 1907, **352**, 13) isolated *d*-usnic acid and a compound which he designated scopuloric acid, m. p. 260°, and which he considered to have the empirical formula $C_{19}H_{16}O_9$ and to form a monoacetate, $C_{21}H_{18}O_{10}$, m. p. 235—236°. This compound does not appear to have been investigated further, but in 1930, having obtained a quantity of authentic *Ramalina scopulorum*, we isolated, along with a small amount of usnic acid (yield, 0·52%), a substance having the properties of Zöpf's scopuloric acid and yielding an acetyl derivative, m. p. 235—236°. The formula of the compound, however, was found to be $C_{18}H_{11}O_8(OMe)$ and the acetyl derivative prepared by Zöpf's method to be a diacetate. In addition a tetra-acetate, a compound which appears to be a *dianil*, a hydration *product*, and two methylation *products* were obtained. Dry distillation of the substance gave rise to atranol monomethyl ether and fusion with potassium hydroxide yielded orcin and a compound which appeared to be 2 : 6-dihydroxy-*p*-toluic acid.

As a result of their work on stictic acid Asahina and his co-workers (*Ber.*, 1933, **66**, 1080) suggested that this compound was probably identical with Zöpf's scopuloric acid, a view which appeared to be in agreement with our experimental findings except that the properties of both the monoanil and the di-stictic acid anilide described by the Japanese authors (*Ber.*, 1933, **66**, 943; 1934, **67**, 1968) differed from those of the dianil which we obtained. Further, by the action of cold aqueous potassium hydroxide, scopuloric acid readily yielded the aforementioned hydration product, which on treatment with acetic anhydride and pyridine underwent simultaneous dehydration and acetylation, yielding the diacetate, m. p. 235—236°.

Having obtained an authentic specimen of stictic acid from *Lobaria pulmonaria*, for which we are indebted to Professor Asahina, we have now made a detailed comparison of the two acids and their respective derivatives, including the dianils, and found them to be identical in every way. Accordingly, since stictic acid was discovered and named first (Knop and Schnedermann, *J. pr. Chem.*, 1846, **39**, 367), we propose that the name scopuloric acid should be abandoned.

The formation of the hydration product *stictinic acid* we consider to be substantial evidence for the presence of a lactone ring in stictic acid, the existence of which has been deduced by Asahina and his co-workers (*loc. cit.*).

In connexion with the occurrence of stictic acid it is of interest to observe that from Japanese *Ramalina scopulorum* (Retz.) Nyl. Asahina and Yanagita (*Ber.*, 1934, **67**, 803) isolated the closely related salazic acid.

EXPERIMENTAL.

Stictic Acid from Ramalina scopulorum.—The ground lichen * (1478 g.) was extracted (Soxhlet) with acetone for 15 hours and after evaporation of the solvent the residue was digested with warm benzene (or chloroform) to remove a small amount of usnic acid together with oils and waxes. A filtered solution of the residual crude stictic acid (27 g.) in acetone was evaporated on the steam-bath until solid began to separate and then kept for several days. The material (19·8 g.) which separated, m. p. 260° (decomp.), was recrystallised twice from acetone or acetic acid and then from acetone and obtained in clusters of colourless needles, m. p. 270° (decomp.) after sintering at 258°, which did not contain solvent of crystallisation [Found in material dried in a vacuum over phosphoric oxide: C, 59·1; H, 3·8; OMe, 7·9. Calc. for $C_{18}H_{11}O_8(OMe)$: C, 59·1; H, 3·6; OMe, 8·0%]. It separated from 80% aqueous acetone as a crystalline powder, which appeared to be the dihydrate, having the same m. p. (Found: C, 54·5; H, 4·5; OMe, 8·0; H_2O, 7·9. Calc. for $C_{19}H_{14}O_9,2H_2O$: C, 54·0; H, 4·3; OMe, 7·4; H_2O, 8·5%). The crystalline form, alcoholic ferric chloride reaction (purple with one drop, changing to brown on addition of several drops of the reagent), the solubilities in organic solvents, and the behaviour with alkalis of this compound were identical with those of authentic stictic acid. Mixed with the latter, it showed no depression of the m. p.

The diacetate, prepared by refluxing the acid (0·75 g.) with acetic anhydride (25 c.c.) for $\frac{3}{4}$ hour, separated from acetic acid in clusters of colourless needles, m. p. 235—236°, undepressed by admixture with an authentic specimen (Found: C, 58·5; H, 3·7. Calc. for $C_{23}H_{18}O_{11}$: C, 58·7; H, 3·8%).

The clear solution obtained by agitating a mixture of stictic acid (1 g.) and acetic anhydride (10 c.c. containing a drop of concentrated sulphuric acid) was kept for 14 hours and then mixed with excess of water. The resulting tetra-acetate crystallised from dilute acetone in colourless laminae, m. p. 226—227° (Found: C, 57·1; H, 4·2. Calc. for $C_{27}H_{24}O_{14}$: C, 56·7; H, 4·2%). The tetra-acetate obtained from authentic stictic acid had m. p. 223—224° and a mixture of the two products melted at 224° (Asahina and co-workers, *loc. cit.*, give m. p. 221—222°).

Stictic Acid Dianil.—On warming a suspension of the acid (0·3 g.) from *Ramalina scopulorum* in alcohol (20 c.c.) containing aniline (0·5 c.c.) on the water-bath for 1 hour, thick yellow prisms of the *compound* gradually formed, which, after being washed with alcohol and dried, had m. p. 234° [Found: C, 69·1; H, 4·7; N, 5·3; OMe, 5·8. Calc. for $C_{18}H_{11}O_6(OMe)(N{\cdot}C_6H_5)_2$: C, 69·4; H, 4·5; N, 5·2; OMe, 5·8%]. It was sparingly soluble in the usual organic solvents and gave a purple coloration with alcoholic ferric chloride. Agitation of a suspension of this derivative in acetone containing a little concentrated hydrochloric acid regenerated stictic acid, m. p. 270° (decomp.).

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* We are greatly indebted to Professor Raistrick, F.R.S., for a supply of this lichen, which was collected by Miss M. C. Knowles of the National Museum of Ireland, near high water mark in the vicinity of Howth, in March, 1930.

Under the same conditions authentic stictic acid formed the dianil, m. p. and mixed m. p. 234° (Found : C, 69·1; H, 4·9; OMe, 6·0%).

Stictinic Acid.—A solution of stictic acid (4·5 g.) in 10% aqueous potassium hydroxide (100 c.c.) was kept for ¾ hour, acidified with hydrochloric acid, and extracted with ether. Evaporation of the dried extract left *stictinic acid*, which separated from ethyl acetate–light petroleum in clusters of colourless needles (3·9 g.), m. p. 223—224°, which did not lose weight on being dried at 100—110° (Found : C, 56·4; H, 4·2. $C_{19}H_{16}O_{10}$ requires C, 56·4; H, 4·0%). This compound, which is readily soluble in hot ethyl acetate and insoluble in benzene, gives a blue coloration with alcoholic ferric chloride and an unstable yellow coloration with bleaching powder. It dissolves in aqueous sodium bicarbonate with the evolution of carbon dioxide, forming a yellow solution.

Treatment of stictinic acid (0·5 g.) with acetic anhydride (5 c.c.) and pyridine (2·5 c.c.) at 37° for 16 hours gave rise to the diacetate of stictic acid, m. p. and mixed m. p. 234° (Found : C, 58·3; H, 3·8%).

Methylation of Stictic Acid.—A solution of the compound (2 g.) in acetone (50 c.c.) was refluxed with methyl iodide (5 c.c.) and silver carbonate (4 g.) for 1 hour; a sample did not give a ferric chloride reaction. On isolation the *product* separated from ethyl acetate in tiny needles (1·4 g.), m. p. 174° [Found : C, 60·8; H, 4·4; OMe, 21·7. $C_{18}H_9O_6(OMe)_3$ requires C, 60·9; H, 4·4; OMe, 22·5%]. When the silver carbonate was replaced by silver oxide (ferric chloride reaction negative after 1·5 hours), an isomeric *compound* was obtained, which separated from ethyl acetate–ligroin in clusters of colourless slender needles, m. p. 242—243° (Found : C, 60·6; H, 4·5; OMe, 22·7%), moderately soluble in acetone and almost insoluble in warm methyl alcohol or benzene. A mixture of the two ethers began to melt at 163°.

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[*Received, July 18th,* 1935.]