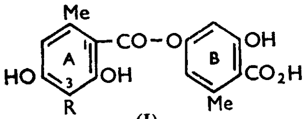
328. *A New Synthesis of Diploschistesic Acid.*

By T. R. Seshadri and G. B. Venkatasubramanian.

Experimental support is provided for the biogenetic view that diploschistesic acid arises from lecanoric acid, by a Gattermann reaction of the latter which gives the 3-aldehyde whence Dakin oxidation affords diploschistesic acid.

Diploschistesic acid (I; R = OH) occurs in the lichens *Diploschistes scruposus* and *D. bryophilus* alongside lecanoric acid (I; R = H).[1] Its constitution, 3-hydroxylecanoric acid, was suggested by Koller and Hamburg [1] as a result of methanolysis and was confirmed by Asahina and Yasue [2] by a synthesis involving a large number of steps.

Diploschistesic acid is the only case in which the C_8 orsellinic unit of part A has an extra 3-hydroxyl group. Several cases are known where the orsellinic unit B has the extra hydroxyl group in the 3'-position and there *meta*-depsides result.



(I)

The biogenesis of these depsides with extra hydroxyl groups has already been discussed.[3] There are two ways by which they can result: (i) by oxidation at the C_8 stage to yield a 3-hydroxyorsellinic acid derivative [4] with subsequent formation of the depside, and (ii) by oxidation after depside formation. In the first case a *meta*-depside should always be formed owing to its greater stability. The ramalinolic acid series could have arisen by such a method.[5] The formation of diploschistesic acid would support the existence of the second mechanism also. This is supported by the co-occurrence of lecanoric acid and diploschistesic acid in the same lichen.[1]

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[1] Koller and Hamburg, *Monatsh.*, 1936, **65**, 367.
[2] Asahina and Yasue, *Ber.*, 1936, **69**, 2327.
[3] Seshadri, *Proc. Indian Acad. Sci.*, 1944, **20**, *A*, 1.
[4] Aghoramurthy and Seshadri, *Proc. Indian Acad. Sci.*, 1952, **35**, *A*, 327.
[5] Asahina and Kusaka, *Ber.*, 1936, **69**, 1896.

The above conclusion has now been verified by the application of *ortho*-nuclear oxidation to lecanoric acid, formation of an aldehyde and subsequent conversion of the aldehyde group into a hydroxyl group. A 3-aldehyde group has now been introduced into lecanoric acid by Gattermann reaction in presence of 2 mols. of aluminium chloride, giving a product shown to have formula (I; R = CHO) by hydrolysis by alkali or acetic acid to atranol and orcinol, and by methanolysis to methyl hæmatommate and orcinol. When a large excess of aluminium chloride was used the depside seemed to undergo preliminary fission followed by a Gattermann reaction, because hæmatommic acid was obtained as the sole product. Dakin oxidation of the 3-formyl-lecanoric acid gave diploschistesic acid (I; R = OH) agreeing in properties with those described by Asahina and Yasue.[2]

EXPERIMENTAL

3-*Formyl-lecanoric acid* (I; R = CHO).—To an ice-cold solution of dry lecanoric acid (6·4 g.) in absolute ether (150 c.c.) containing zinc cyanide (4·8 g.), a solution of anhydrous aluminium chloride (8 g.) in ether (50 c.c.) was gradually added at 0°, and dry hydrogen chloride passed into the mixture for 3 hr. The cyanide slowly dissolved and a semisolid mass separated. After 24 hr. the ether layer was decanted and the residue treated with crushed ice and later heated for ½ hr. at 80°. The solid product was filtered off and several crystallisations from aqueous dioxan yielded 3-*formyl-lecanoric acid* as colourless needles (5 g.), m. p. 174° (decomp.) (Found: C, 58·4; H, 4·4. $C_{17}H_{14}O_8$ requires C, 58·9; H, 4·1%). It readily gave a yellow solution in aqueous sodium hydrogen carbonate, gave a wine-red colour with alcoholic ferric chloride, and readily formed a 2 : 4-dinitrophenylhydrazone.

If, in the above experiment, a large excess of aluminium chloride was employed, the product was hæmatommic acid, m. p. 174°, depressed on admixture with 3-formyl-lecanoric acid. Esterification of the product with methyl sulphate–sodium hydrogen carbonate in acetone gave methyl hæmatommate, m. p. and mixed m. p. 146°. Decarboxylation of hæmatommic acid by boiling with water for 2 hr. gave atranol, m. p. and mixed m. p. 125°.

Fission of 3-*Formyl-lecanoric Acid.*—(a) *With alkali.* The acid (5 g.) was heated in 10% aqueous sodium hydroxide (100 c.c.) on a water-bath for ½ hr. under nitrogen. Acidification with dilute hydrochloric acid gave atranol, m. p. 125°. The mother-liquor was concentrated under reduced pressure and repeatedly extracted with ether. The ether solution was dried (Na_2SO_4) and the solvent distilled off. The residue, crystallised from chloroform, had m. p. 108° alone or mixed with authentic orcinol.

(b) *Fission with acetic acid.* The aldehydo-acid (5 g.) in 90% acetic acid (100 c.c.) was refluxed for 3 hr. Acetic acid was removed under diminished pressure, and water (20 c.c.) added. The whole was shaken and filtered. The residue (2 g.) was atranol, m. p. 125°. The filtrate on evaporation to dryness gave orcinol, m. p. 107°.

(c) *Methanolysis.* The aldehydo-acid (2 g.) in absolute methanol (200 c.c.) containing a trace of sodium hydroxide (20 mg.) was refluxed for 5 hr. Methanol was removed under diminished pressure and water (50 c.c.) added. The solid that separated crystallised from ethanol, giving methyl hæmatommate, m. p. 146°. The filtrate on evaporation to dryness yielded orcinol, m. p. 107°.

Diploschistesic Acid (I; R = OH).—The aldehydo-acid (1 g.) in 4% aqueous sodium hydroxide (6 c.c.) was cooled to 10°. A 6% solution (2·5 c.c.) of hydrogen peroxide was added and the mixture shaken for 1 hr. The solid that separated on acidification with dilute hydrochloric acid was repeatedly crystallised from aqueous acetone, yielding diploschistesic acid as colourless leaflets (0·6 g.), m. p. 170° (decomp.) [Asahina and Yasue reported the m. p. as 174° (decomp.)] (Found: C, 57·4; H, 4·3. Calc. for $C_{16}H_{14}O_8$: C, 57·5; H, 4·2%). It gave a blue-violet colour with alcoholic ferric chloride.

The tetra-acetate, prepared by the method of Asahina and Yasue, crystallised from benzene as prisms, m. p. 164—165° (Found: C, 57·5; H, 4·1. Calc. for $C_{24}H_{22}O_{12}$: C, 57·4; H, 4·4%). Asahina and Yasue reported the same m. p.

DELHI UNIVERSITY, INDIA.

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