CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part IV. Constitution of Montagnetol

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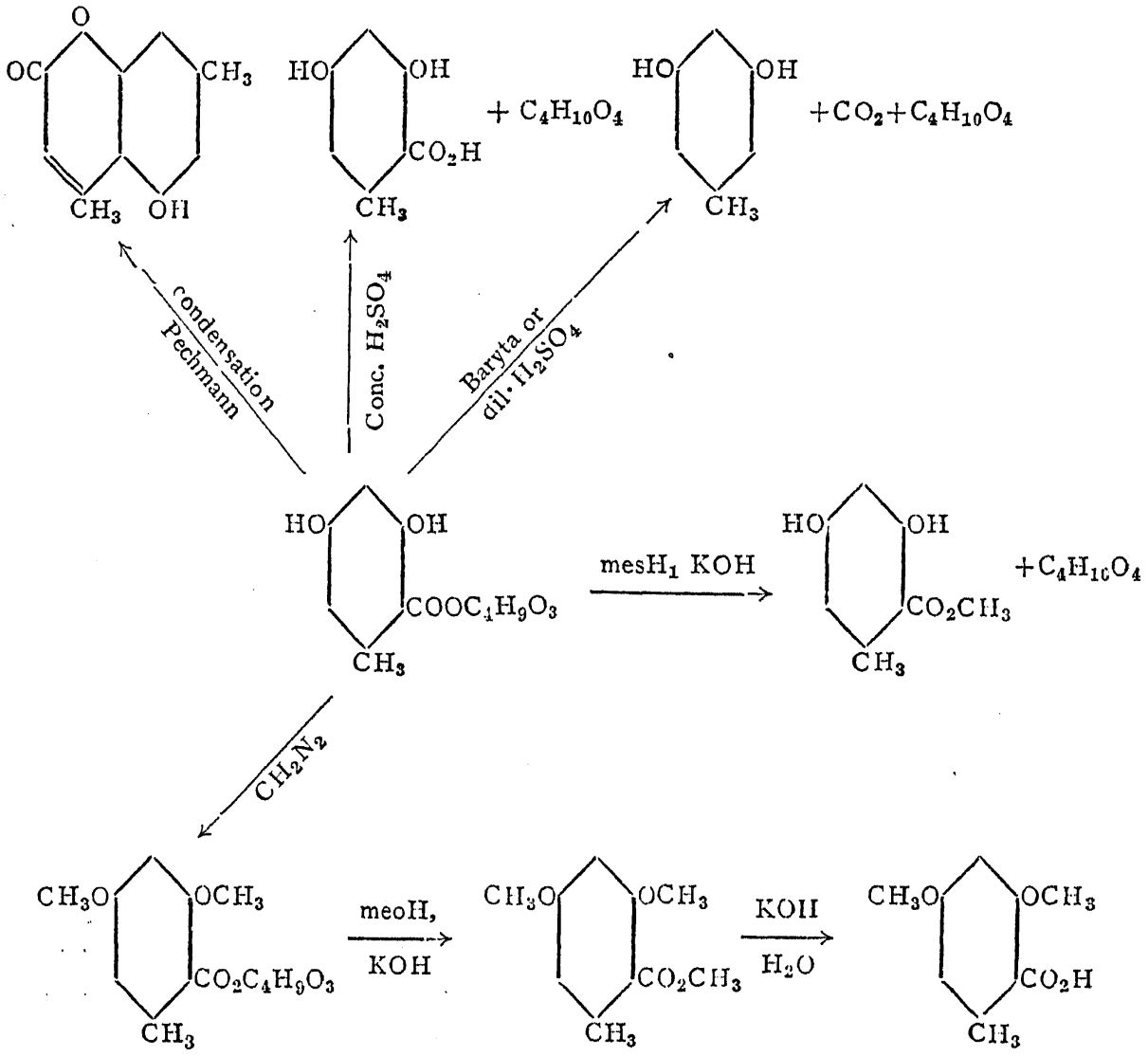
THE isolation of a new phenolic component of *Rocella montagnei* named "Montagnetol" was described in Part III of this series.[1] After further careful purification and analysis its composition was found to agree more closely with the formula, $C_{12}H_{16}O_7$. Though the substance did not give the homofluorescein reaction quickly as does orcinol, when the solution was allowed to stand for a few days the characteristic fluorescence developed. There was thus an indication that montagnetol is a derivative of orcinol. This was supported by the fact that 4: 7-dimethyl-5-hydroxy coumarin was formed, when it was treated with ethylacetoacetate under the conditions of Pechmann's reaction. The idea was followed up by subjecting the compound to the action of aqueous baryta and methyl alcoholic potash and analysing the products of decomposition. Decomposition with boiling aqueous baryta took place very readily yielding barium carbonate, orcinol and (meso) erythritol. With methyl alcoholic potash, however, the methyl ester of orsellinic acid was produced along with erythritol. Further by the action of concentrated sulphuric acid in the cold, pure samples of orsellinic acid and (meso) erythritol could be obtained. Dilute sulphuric acid in the cold had no action on the compound; but when the mixture was boiled, decomposition resulted, orcinol and erythritol being formed. From all these data it could be deduced that montagnetol is a compound of orsellinic acid and erythritol and since it is a neutral body it should be the erythrityl ester of orsellinic acid. That none of the phenolic hydroxyl groups are involved in any combination with erythritol was established as follows:—

Montagnetol was methylated with excess of diazomethane and the product was directly treated with methyl alcoholic potash. By this means the dimethyl ether of methyl orsellinate was obtained and this on hydrolysis yielded dimethyl ether of orsellinic acid. It is therefore definitely established that the above conclusion regarding the constitution of montagnetol is correct. The reactions taking place can be represented as below:



The discovery of montagnetol and a knowledge of its constitution bring out prominently a number of interesting features: (1) Orsellinic acid has so far not been detected in lichens though depsides containing this unit are common. It has now been shown that its ester with a sugar alcohol occurs in appreciable quantities. Obviously the instability of the free acid and the stability of the ester account for this phenomenon; (2) Though methyl esters of lichen acids are known to occur fairly frequently in nature, montagnetol seems to be the first definite instance of ester formation with a sugar alcohol. In this connection analogy between montagnetol and the esters of digallic acid with glucose (involving the alcoholic hydroxyl groups) which are widely present in gallotannins may be pointed out.

Experimental

Properties of Montagnetol.—Some of the properties of montagnetol have already been described in a previous communication. It has been stated therein that it does not give the homofluorescein reaction readily when heated with chloroform and alkali. However, it was noticed that the solutions, when

kept for a number of days, gradually developed the characteristic greenish-yellow fluorescence. Montagnetol formed no precipitates with lead acetate, either basic or neutral. With bleaching powder it gave a bright red colour similar to that given by orcinol, lecanoric acid and erythrin. Potassium permanganate solution and Fehling's solution were both reduced by the compound. The colour of Schiff's reagent was not restored. The compound was slightly bitter to taste. A pure sample melted at 156–57°. It crystallised from acetone-benzene mixture as large rectangular tablets; when mounted with a drop of water on a slide they appeared as lense-shaped crystals. [Found: C, 53·0; H, 5·8; $C_{12}H_{16}O_7$ requires C, 52·9; H, 5·9%.]

Condensation of montagnetol with aceto-acetic ester.—A mixture of montagnetol (1 g.) and aceto-acetic ester (3 c.c.) was cooled in freezing mixture, treated with concentrated sulphuric acid (4 c.c.) and left for 24 hours at 0°. The reaction product was then poured into ice-water with good stirring. A slimy substance was obtained, which could be filtered only very slowly. It could not be crystallised and obtained pure. It was therefore treated with 10 c.c. of potassium hydroxide (10%) and left at the room temperature for 24 hours. The solution was then acidified and the precipitated solid filtered and recrystallised from alcohol, when it was obtained in the form of long fine needles melting at 257–58°. The compound gave no colour with ferric chloride, and dissolved only partly in sodium carbonate solution and completely in sodium hydroxide, with a yellow colour. It was found to be identical with an authentic specimen of 5-hydroxy-4: 7-dimethyl coumarin, the mixed melting point being undepressed.

Fission of montagnetol with baryta water.—Montagnetol (0·5 g.) was refluxed with baryta water (8%, 20 c.c.) for 2 hours. A bulky precipitate separated out in 5 minutes and did not dissolve subsequently. It was filtered off and washed with small quantities of water. It was found to be in the form of fine, small needles and was identified as barium carbonate.

The filtrate from above was shaken with ether, but the ether did not extract any material. The aqueous solution was then rendered slightly acid with dilute sulphuric acid and the precipitated barium sulphate filtered off. The filtrate was repeatedly extracted with ether and then neutralised by treatment with excess of barium carbonate. The ether extracts were combined and concentrated, when a red viscous liquid (L) was obtained. The aqueous solution obtained after filtering off the barium carbonate and sulphate, was concentrated, whereby a residue (E) was obtained. On washing repeatedly with ether (E) solidified to a red mass; when a sample of this was treated with a drop of water on the porous plate it became colourless

and melted at 121°. It crystallised from water in the form of hexahedral prisms and possessed a sweet taste and was found to be identical with meso-erythritol by comparison with an authentic specimen. Yield: 0·2 g.

The red viscous liquid (L), on being inoculated with a small crystal of orcinol, quickly turned into a crystalline solid. It was in the form of needles and melted at 55–57° C. and gave the homofluorescein reaction. Mixed melting point with an authentic specimen of orcinol was un-depressed. Yield: 0·2 g.

Fission with methyl acloholic potash.—Montagnetol (0·5 g.) was dissolved in methyl alcoholic potash (4%—20 c.c.) and the solution refluxed gently for two hours on a water-bath. Care was taken to see that the temperature of the bath did not rise above 70° C. The solution was then diluted with an equal volume of water and shaken with ether. No material was, however, extracted by the ether. The aqueous portion was then acidified with hydrochloric acid and again ether extracted. The ether extract was separated and concentrated when a brownish-yellow solid was obtained. On treatment with sodium bicarbonate solution only a very small portion went into solution while the rest was undissolved. The mixture was filtered and the insoluble residue washed thoroughly with water. The solid was then recrystallised from acetone, when it was obtained in the form of rhombic crystals which when spread on a microscope slide and treated with a drop of methylated spirit appeared as bundles of long flat needles. It gave a violet colour with ferric chloride and melted at 140–42°. [Found: C, 54·1; H, 6·4; $C_9H_{10}O_4$, H_2O requires C, 54·0; H, 6·0%.] From these results the compound was identified as methyl orsellinate. Its identity was further established by comparison with a pure specimen obtained from lecanoric acid by following the same method of treatment.

The bicarbonate solution obtained above was acidified and extracted with ether. The ether extract on concentration yielded a very small amount of a sticky residue from which no pure product could be isolated.

Fission with cold concentrated sulphuric acid.—Montagnetol (0·2 g.) was dissolved in cold concentrated sulphuric acid (1 c.c.) and the solution kept overnight in the refrigerator. It was then poured into a small quantity of ice-cold water (10 c.c.) and the precipitated solid filtered off and washed well with water. When recrystallised from acetone-ether-benzene mixture, it was obtained in the form of clusters of needles melting at 176° with decomposition. [Found: C, 51·9; H, 5·4; $C_8H_8O_4$, H_2O requires C, 51·6; H, 5·4%.] It gave a violet colour with ferric chloride and was found to be a carboxylic acid, carbon dioxide being briskly evolved from a solution of

sodium bicarbonate when the substance was added to it. From these reactions and the analytical values the compound was identified as orsellinic acid and was found to be identical with an authentic specimen of orsellinic acid obtained by the above method of hydrolysis from lecanoric acid.

Action of dilute sulphuric acid on the compound.—There was no change when montagnetol was treated with cold dilute sulphuric acid, but it underwent degradation when the hot acid was employed, as indicated below:

Montagnetol (2 g.) was refluxed with 7% sulphuric acid (30 c.c.) for 6 hours on the wire-gauze and after cooling, the solution was ether extracted. The ether extract on concentration gave orcinol, which was identified by the homofluorescein reaction and by comparison with an authentic specimen. The aqueous solution was neutralized by treatment with excess of barium carbonate and the solid filtered off. On concentration, the filtrate gave a sticky solid which could be separated into two fractions. A portion went into solution in a mixture of acetone and ether (1 : 1) and on concentrating the solution, was obtained in the form of colourless crystals melting at 154°. This was found to be the unchanged montagnetol. The other portion, insoluble in acetone-ether mixture, melted at 120–22° after purification by recrystallisation from acetone and was found to be identical with an authentic specimen of meso-erythritol.

Methylation of montagnetol with diazomethane.—Montagnetol (1·0 g.) was dissolved in the minimum quantity (20 c.c.) of absolute methyl alcohol and to this solution excess of ethereal diazomethane (1·5 g. contained in 100 c.c. of ether) was added in small quantities at a time during the course of two days. The mixture was kept at the room temperature for about a week. The liquid was then filtered and the solvents distilled off. A viscous liquid was left behind and it could not be converted into a crystalline condition. It gave no colour with ferric chloride either in the aqueous or alcoholic solution.

The viscous liquid was treated directly with 20 c.c. of methyl alcoholic potash (4%) and the solution refluxed gently on a water-bath for 2 hours. The contents were then diluted with an equal amount of water when the clear solution became turbid, with the separation of an amorphous white solid. The whole mixture was, however, ether-extracted and the ether solution cencentrated when a viscous pale yellow liquid was obtained. The aqueous solution was now acidified and again ether-extracted when some more of the viscous liquid was obtained. The two portions were mixed and gently heated on the water-bath for about 15 minutes with 10 c.c. of 5% sodium hydroxide; about 5 c.c. of alcohol were added to obtain complete solution of the substance. The liquid was left overnight when a small

amount of resin separated. It was filtered off and the filtrate ether-extracted whereby a small amount of an oily impurity was also removed. The aqueous portion was then acidified and again extracted with ether. The ether extract on concentration yielded a crystalline solid which after recrystallisation from alcohol appeared as colourless prisms and melted at 140–41° with decomposition. It gave no colour with ferric chloride and was acidic in nature. [Found: C, 60·6; H, 6·2; $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%.] The acid was therefore identified as the dimethyl ether of orsellinic acid (melting point given in the literature is 140° with decomposition). The yield was almost quantitative.

Summary

The constitution of montagnetol has been established as the erythrityl ester of orsellinic acid for the following reasons: (1) it gives the homofluorescein reaction slowly, (2) 5-hydroxy-4: 7-dimethyl coumarin could be obtained as a product of its condensation with ethylacetoacetate under the conditions of Pechmann's reaction, (3) decomposition with hot dilute sulphuric acid or with hot baryta produces orcinol and erythritol, (4) concentrated sulphuric acid at 0° gives orsellinic acid and erythritol, (5) hot methyl alcoholic potash converts it into methyl orsellinate and erythritol, and (6) by the action of diazomethane followed by methyl acloholic potash dimethyl ether of methyl orsellinate is obtained.

REFERENCE

1 Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1941, **13**, 199–202.