CCXLVIII.—*The Treatment of Cedrene with Mercuric Acetate.*

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AQUEOUS mercuric acetate has proved of considerable value in investigations of the structures of certain terpenes and sesquiterpenes (compare Balbiano and Paolini, *Ber.*, 1902, **35**, 2994; Henderson and Agnew, J., 1909, **95**, 289; Deussen, *J. pr. Chem.*, 1926, **114**, 63). It has now been found that cedrene reacts slowly with this reagent, mercurous acetate being precipitated. The aqueous solution contains an amorphous *organo-mercury* compound, which is slightly soluble in ethyl alcohol and insoluble in most other organic solvents with the exception of glacial acetic acid and chloroform.

Owing to the insolubility of this primary product, it is impossible to replace the acetoxy-group by halogens, since addition of an alkali halide to a solution in alcohol containing a little acetic acid reprecipitates the original compound. These observations show that it is not a true acetoxymercuri-derivative of the sesquiterpene (compare Deussen, *loc. cit.*). The compound is purified by precipitation from chloroform solution by addition of ether. Analysis indicates $C_{16}H_{28}O_6Hg_2$ as the most probable formula, suggesting that it is a mixture of two or more derivatives, the separation of which is impossible owing to their amorphous nature.

In investigating the oxidation of pinene with mercuric acetate, Henderson and Agnew (*loc. cit.*) obtained the same oxidation products by the action of mercuric oxide in glacial acetic acid. In the case of cedrene, there is some resinification during the reaction, but a mercury-free oxidation product is obtained. This consists of an *alcohol.* The formula $C_{15}H_{24}O$ is indicated by analysis, but a tricyclic alcohol of this composition would be unsaturated, whilst the above oxidation product is fully saturated and therefore should have the formula $C_{15}H_{26}O$. A similar observation has been made by Henderson and Sword (unpublished work) who obtained a saturated alcohol by oxidation of cedrene with hydrogen peroxide. Analysis of this alcohol also indicated the formula $C_{15}H_{24}O$ rather than $C_{15}H_{26}O$. These two products are apparently identical with the tertiary alcohol, pseudo-cedrol, isolated by Semmler (*Ber.*, 1912, **45**, 1384) from cedar-wood oil.

EXPERIMENTAL.

Treatment of Cedrene with Mercuric Acetate.—Cedrene (28 g.) was added to a solution of mercuric acetate (86 g.) in water (400 g.) and kept for five or six weeks with occasional shaking. At the end of that time the aqueous liquor was filtered from mercurous acetate, extracted repeatedly with chloroform, and the extract washed and dried. After removal of the greater part of the chloroform by evaporation, ether was added, and the product precipitated as a fine yellow powder, which was filtered off and dried on porous pot. After several reprecipitations it melted at 193—195° (decomp.). Under a pressure of 1—2 mm. the mercury compound could be heated to 280° without melting, though slight darkening occurred in the region of 240°. Some decomposition took place, for beads of metallic mercury were observed and the characteristic smell of cedrene was perceptible on opening the tube. The compound gave the cacodyl test, showing the presence of the acetoxy-group (Found : C, 26·5; H, 3·55; Hg, 57·5. $C_{16}H_{28}O_6Hg_2$ requires C, 26·8; H, 3·9; Hg, 55·9%).

Oxidation of Cedrene with Mercuric Oxide.—Mercuric oxide (24 g.) was added in small quantities to a solution of cedrene (20 g.) in glacial acetic acid (200 c.c.) at 60—70°; metallic mercury soon began to separate, and the reaction appeared complete after about four hours. The mercury was filtered off, the filtrate diluted with an equal volume of water, neutralised with sodium carbonate, and extracted with ether. The brownish oil thus obtained gave, on distillation, two fractions : (*a*) b. p. 125—130°/10 mm. and (*b*) b. p. 140—150°/10 mm. Fraction (*a*) was proved to be cedrene by examination of its physical constants : $d_{4^\circ}^{20^\circ}$ 0·9504; $n_D^{20^\circ}$ 1·5020. Fraction (*b*), which appeared to be an *alcohol,* had $d_{4^\circ}^{20^\circ}$ 0·9872; $n_D^{20^\circ}$ 1·5071, $[R_L]_D$ 66·9 (Calc. for a tricyclic sesquiterpene alcohol, 66·4) (Found : C, 81·5; H, 10·7. $C_{15}H_{26}O$ requires C, 81·3; H, 11·7. $C_{15}H_{24}O$

requires C, 81·9; H, 10·9%). The alcohol was fully saturated towards bromine. No crystalline *p*-nitrobenzoate or phenylurethane was obtained.

I desire to take this opportunity of expressing my thanks to Professor G. G. Henderson, F.R.S., for his continued encouragement and advice.

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[*Received, July 4th*, 1930.]