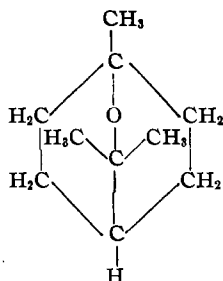


NEW MOLECULAR COMPOUNDS OF EUCALYPTOL.

BY FRANCIS D. DODGE.*

Cineol, or eucalyptol, as it is more generally called, a cyclic ether having the formula:



is remarkable for the variety of molecular compounds which it forms with acids, phenols and salts. A list of these has been given by Muller.¹

The acids which so far have been found to yield crystalline compounds are: HCl, HBr, HI, H₃AsO₄, H₃PO₄, ferro- and ferricyanic, cobalti- and platinocyanic, oxalic and ortho-coumaric acids, and the arsenic and phosphoric compounds have been utilized for the determination of eucalyptol in the various oils of which it is a constituent.

Phenol compounds have been obtained with phenol, the three cresols: catechol, resorcinol and hydroquinone; pyrogallol, thymol, alpha and beta naphthol; the resorcinol and ortho-cresol compounds have also found application in analytical methods.

Other compounds not listed by Muller are those with 1.5 dioxy-naphthalene,² and with meta-nitro-benzaldehyde.³

The list of phenolic compounds, however, appears to be by no means exhausted, and has been extended a little by the addition of the following, prepared by the writer.

Eucalyptol and Ortho-Chlor-Phenol.—On dissolving 6 Gm. *o*-chlor-phenol in 20 Gm. warm eucalyptol, the compound crystallized in large prisms, on cooling. Melting point: 57–59°. Analysis: 6.667 Gm. dissolved in an excess of 10% NaOH, in a "cassia" flask, yielded eucalyptol, 3.6 Gm. or 54%. (Calc. for C₆H₄ClOH. C₁₀H₁₈O, 54.5%.)

Eucalyptol and Ortho-Brom-Phenol.—Five grams *o*-brom-phenol, dissolved in 20 Gm. eucalyptol, yielded about 8 Gm. of transparent prisms, melting at 75.5–76° (uncorr.). Analysis: 1.903 Gm., dissolved in 5 ml 10% NaOH, yielded 0.88 Gm. eucalyptol, or 46.2%. (Calc. for C₆H₄BrOH. C₁₀H₁₈O, 47.1%.)

Eucalyptol and Ortho-Iodo-Phenol.—Preparation as in the case of *o*-brom-phenol. Yield 7.5 Gm. Melting point: 89–89.5° (uncorr.). Analysis: 1.889 Gm. yielded 0.739 eucalyptol, or 39%. (Calc. for C₆H₄IOH. C₁₀H₁₈O, 41.1%.)

The three compounds are thus analogous in composition to the ortho-cresol compound.

* Scientific Section, A. P. H. A., Toronto meeting, 1932.

¹ *Riechst. Ind.*, 4 (1929), 143.

² *Pharm. Zentr.* (1912), 32.

³ *Centr. Bl.*, 1 (1893), 657.

Eucalyptol and Para-Hydroxy-Benzoic Acid.—Preparation like the previous compound. Yield, about 7 Gm. of long prisms which lose eucalyptol rapidly on exposure, and melt, with decomposition, at 63–65°. Analysis: 2.29 Gm. dissolved in alcohol required 10.8 ml 0.5 *N* KOH, equivalent to 0.745 Gm. *p*-hydroxy-benzoic acid, or 32.5%. (Calc. for $C_6H_4OH.CO_2H.C_{10}H_{18}O$, 47.2% acid. Calc. for $C_6H_4OH.CO_2H.2C_{10}H_{18}O$, 30.9% acid.)

The analysis is not very exact, owing partly to the ready dissociation of the compound, and also to the fact that the acid yields high figures on titration, due to the presence of the hydroxyl group. The conclusion, however, appears justified, that the compound is analogous to those with resorcinol and hydroquinone, which contain two molecules of eucalyptol to one of the phenol.

The preparation of molecular compounds with tri-brom-, tri-chlor-, tri-nitro-phenol; guaiacol, eugenol and isoeugenol; salicylic, meta-hydroxybenzoic, anisic, veratric, ortho-, meta-, para-nitrobenzoic or anthranilic acids; ortho- or para-hydroxy-benzaldehyde was unsuccessful.

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FURTHER OBSERVATIONS UPON THE BROMINE METHOD FOR THE ESTIMATION OF ALKALOIDS.

BY H. B. HAAG.*

Several years ago Weiss and Hatcher (1) described a method for the quantitative estimation of quinine and quinidine, both in pure solutions and in tissue extracts. The adaptability of this test depends upon the fact that these alkaloids promptly decolorize diluted bromine water by uniting chemically with the bromine with resulting disappearance of the yellow color.

This summer, while working in the Department of Pharmacology of Cornell University Medical College, New York City, the thought occurred that this procedure might be extended to include other common alkaloids and related compounds. The technic employed was essentially identical to that previously outlined by Weiss and Hatcher. Diluted bromine water was prepared by diluting a saturated aqueous solution ten times with distilled water. It was concluded from several tests that this diluted bromine solution, when kept in a glass-stoppered bottle, did not rapidly deteriorate and hence the freshly diluted preparation certainly retained, for purposes of this test, its original concentration for at least several hours. The standard solution of the alkaloid was prepared so that each cubic centimeter corresponded to 1.0 mg. of the alkaloidal base, and was made up in 0.5% sulphuric acid. In this connection it should be mentioned that all solutions tested against the bromine water should be acid, as alkalies themselves decolorize the solution. The bromine water was standardized against this known solution as follows: 0.5 cc. of the diluted bromine water, accurately measured, was placed in a test-tube of about 5 cc. capacity, and then the standard was gradually added from a micro-pipette until complete decolorization of the bromine water had taken place, as viewed by reflected light against a white background. This was repeated so that an average value could be obtained from several fairly

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