

PHENOLIC ESTERS OF *p*-METHOXYCINNAMIC ACID.*

BY C. W. SONDERN.

The acid used in the experiments here described was obtained from its natural ethyl ester separated from the oil of *Kampferia Galanga* L. This oil had been prepared at the Botanical Garden at Buitenzorg, Java, to the Director of which thanks are due for his kind coöperation. The oil had been distilled for the purpose of securing a somewhat larger amount of *n*-pentadecane, first isolated by van Romburgh. However, since the oil consists largely of the handsomely crystallizable ethyl ester of *p*-methoxycinnamic acid it seemed desirable to use this material for further study of its derivatives.

Guaiacol Ester.—The method followed was the one successfully employed by P. A. Foote (1). A mixture of 5 Gm. of acid, 3.5 Gm. of liquid guaiacol and 2.4 cc. of phosphorus trichloride in 80 cc. of anhydrous toluene was refluxed gently first in a water-bath for an hour, then in an oil-bath for another hour. The toluene having been removed by distillation under diminished pressure, the reaction product was washed with 5% aqueous KOH to remove any excess acid or phenol. The residue when recrystallized from alcohol yielded 4.5 Gm. (57% of theoretical yield computed on the acid used) of a product melting at 102–103°. Upon saponification, duplicate determinations yielded values of 181 and 188. The theoretical saponification value is 186. The acid regenerated from the saponification liquid melted at 170°, the m. p. of *p*-methoxycinnamic acid. Guaiacol was identified in the saponification liquid by means of the ferric chloride test.

α -Naphthol Ester.—The same process applied to α -naphthol yielded a crystalline product, but the yield was low, viz., 22%. Recrystallized, it melted at 102°. Upon saponification, duplicate determinations yielded 197 and 180, respectively. The computed S. V. is 184. The regenerated acid melted at 170°. The α -naphthol recovered melted at 90°, the recorded m. p. being 94°, and gave a positive test with ferric chloride.

Resorcinol Esters.—An attempt to prepare resorcinyll paramethoxycinnamate using phosphorus trichloride as the condensation agent resulted in the formation of large amounts of resinous by-products. To remedy this, phosphorus pentoxide (2) was used.

(I) Three and three-tenths grams of the acid and 2.1 Gm. of resorcinol were dissolved in approximately 60 cc. of toluene together with 1.2 Gm. of phosphorus pentoxide. The mixture was refluxed on an oil-bath for two hours and then the toluene was distilled off under diminished pressure. The product was washed with 5% aqueous KOH to remove any free acid, phenol or mono-ester. The residue, crystallized from hydro-acetone solution, yielded 0.5 Gm. of a product melting at 172–173°. In order to examine this further a larger quantity of material was prepared.

(II) Five grams of *p*-methoxycinnamic acid and 3.2 Gm. of resorcinol were dissolved in approximately 80 cc. of toluene together with 2 Gm. of phosphorus pentoxide. The mixture was refluxed on an oil-bath for two hours and then the toluene was distilled off under diminished pressure. The residue in the distilling flask was washed with 5% aqueous KOH and the product removed and dried in a desiccator over CaCl₂. When crystallized from a hydro-acetone solution and dried, it yielded a light orange crystalline product weighing 1.51 Gm. and melting at 171–172°.

The products from the two experiments were combined and recrystallized. Yield 1.84 Gm., m. p. 173–173.5°. Duplicate saponifications on this product

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yielded values, 259 and 256. The theoretical saponification value for the di-ester is 261. Analysis of the saponification liquor yielded *p*-methoxycinnamic acid m. p. 170° and resorcinol m. p. 115°.

An attempt was made to isolate the mono-ester from the alkaline washings obtained from the above experiments.

The alkaline solution was carefully neutralized with 10% HCl and the neutral solution extracted several times with ether in order to remove any unreacted resorcinol along with the mono-ester. When the aqueous solution was acidified a small amount of impure *p*-methoxycinnamic acid was recovered. The ether-soluble fraction was concentrated and the product dried. A few red crystals melting at 135–137° (with decomposition) were obtained. The quantity of this product was too small to permit its characterization.

REFERENCES.

- (1) *Jour. A. Ph. A.*, 17, 958 (1928).
- (2) M. Bakunin, *Gazz. chim. ital.*, 34, 178 (1902).

THE ADDITION OF STRONG HYDROGEN PEROXIDE IN THE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS.*

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INTRODUCTION.

The amount of nitrogen in some organic compounds is determined successfully by the Gunning or Kjeldahl methods. These two methods have advantages over the Dumas method because of the ease of manipulation and the use of less expensive apparatus. However, the distillation methods are subject to certain limitations because the results in the analysis of compounds containing such groups as nitro, nitroso, azo, azoxy, etc., are inconsistent. Many organic compounds also require a very long period of heating in order to liberate all of the nitrogen.

The investigation reported in this communication was undertaken in order to determine accurately the amount of time saved and the accuracy obtainable when thirty per cent hydrogen peroxide was used in the determination of nitrogen. In the last few years, a number of investigators (1–10) have found hydrogen peroxide to be a valuable oxidizing agent in the decomposition of organic substances, because it hastens the process of digestion and cuts down foaming.

EXPERIMENTAL.

The method employed in the investigation reported in this paper was the Gunning modification of the original Kjeldahl method, which is official with the Association of Official Agricultural Chemists (11). Twenty-five hundredths gram of the organic compound was placed in each of two digestion flasks with ten Gm. of nitrogen-free potassium sulphate and twenty cc. of concentrated sulphuric acid. The contents of both flasks were digested over electrically heated plates, all units of which were of the same construction and gave the same amount of heat. During the digestion, one cc. of a 30 per cent solution of hydrogen peroxide was added to one of the flasks at intervals of ten minutes. The contents of the other flasks were allowed to digest without the addition of the hydrogen peroxide. Each sample was heated until the liquid in the flask was light

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