plants[20] and first applied to paper chromatography by Fink, *et al.*[21] This technique was adapted and extensively used by Benson, *et al.*,[9] for the identification of photosynthetic products. Since the salt necessary to maintain the chloroplasts in an active state interfered with the chromatograms, the extracts were further treated by passing them through a column of Amberlite IR-100 (hydrogen form). The column, about 15 cm. long and 2 cm. in diameter, was prepared by gravity sedimentation of an aqueous suspension of the resin.

The sample to be desalted (about $^9/_{10}$ of the soluble fraction) was diluted with water to 50 ml. and passed through the column at a rate of 2–3 ml. per min. The column was then washed with water (150 ml.) at a similar rate of flow, and the combined eluate and washings, representing the "acid plus neutral" fraction, was evaporated to a small volume (0.7 ml.) at 30° under reduced pressure. The "basic" fraction, which was adsorbed on the resin, was eluted with aqueous ammonia (approx. 2 *N*). The elution was continued until ammonia could be detected in the eluate. The eluate of the "basic" fraction was reduced in volume in the same way as the "acid plus neutral" fraction. Aliquots of the desalted fractions were used for paper chromatography. The "acid plus neutral" fraction contained phosphorylated sugars and organic acids and the "basic" fraction contained the amino acids.

Dihydroxyacetone, alanine, glycine, aspartic acid, malic acid and glycolic acid were identified by cutting out spots from the paper and co-chromatographing with authentic samples of these compounds in the phenol water and butanol–acetic acid mixtures. Identity of the unknown with the authentic compound was evidenced by the appearance of a single spot. Additional evidence for the identity of the amino acids was obtained after deaminating a sample of radioactive material, mixed with carrier, by treatment with a mixture of KNO_2 and glacial acetic acid. The resulting hydroxy acids were then identified by co-chromatography on paper.

Sugar phosphates were identified by eluting the radioactive material from the paper, adding to the eluate 0.05 ml. of 0.2 *M* tris-(hydroxymethyl)-aminomethane buffer, *p*H 8.8, and 0.2 ml. of a solution of alkaline phosphatase (General Biochemicals, 4 mg. per 10 ml.), then incubating at 38° for two to three hours. The phosphatase treated material was then co-chromatographed with authentic sugars.

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[20] D. I. Arnon, P. R. Stout and F. Sipos, *Amer. J. Bot.*, **27**, 791 (1940).

[21] R. M. Fink, D. E. Dent and K. Fink, *Nature*, **160**, 801 (1947).

NOTES

Unsaturated Phenols. II.[1] Attempted Syntheses of *o*-Vinylphenol

BY ALFRED R. BADER

RECEIVED MARCH 25, 1955

As part of a more extensive study of unsaturated phenols, small quantities of *o*-vinylphenol were required. At least five apparently convenient syntheses are described in the literature: (i) the reaction of phenol with ethylene oxide,[2] (ii) the sulfuric acid-catalyzed rearrangement and dehydration of β-phenoxyethanol,[2] (iii) the reaction of vinyl acetate with phenol,[3] (iv) the decarboxylation of *o*-hydroxycinnamic acid,[4] and (v) the thermal decomposition of the benzodioxin obtained from phenol and acetaldehyde.[5]

Smith and Niederl claimed that phenol and ethylene oxide react in the presence of sulfuric acid to give a 65% yield of *o*-vinylphenol, characterized by its tetrabromide and phenoxyacetic acid reported previously.[4b] Many attempts to repeat the work of Smith and Niederl were unsuccessful. The ultraviolet spectrum of the crude reaction product, mainly unreacted phenol, showed no conjugated unsaturation. The crude reaction product was brominated, and the bromophenols were separated by chromatography; no tetrabromide, easily obtained from *o*-vinylphenol, could be isolated.

Smith and Niederl[2] postulated β-phenoxyethanol as the intermediate in the formation of *o*-vinylphenol from phenol and ethylene oxide. Support for this was found in the alleged reaction of β-phenoxyethanol with sulfuric acid at room temperature to yield *o*-vinylphenol. Actually, β-phenoxyethanol is recovered unchanged from the reaction conditions described (identical infrared spectra and physical constants).[6]

The reaction of vinyl acetate with phenol in the presence of sulfuric acid has been reported[3] to yield a polymer from which *o*-vinylphenol has been alleged to be easily obtainable by thermal depolymerization. The product of the very vigorous reaction is a polymer, but no *o*-vinylphenol could be obtained therefrom.

The decarboxylation of *o*-hydroxycinnamic acid[4] provides a convenient method for the preparation of *o*-vinylphenol.

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[1] For paper I see THIS JOURNAL, **75**, 5967 (1953).

[2] R. A. Smith and J. B. Niederl, *ibid.*, **53**, 806 (1931).

[3] J. B. Niederl, R. A. Smith and M. E. McGreal, *ibid.*, **53**, 3390 (1931).

[4] (a) H. Kunz-Krause and P. Manicke, *Arch. Pharm.*, **566**, 555 (1929); (b) K. Fries and G. Fickewirth, *Ber.*, **41**, 367 (1908).

[5] E. Adler, H. v. Euler and G. Gie, *Arkiv Kemi, Mineral., Geol.*, **16A**, No. 12, 1 (1943); *C. A.*, **38**, 5839 (1944).

[6] Adler, *et al.*,[5] also were unable to obtain *o*-vinylphenol from β-phenoxyethanol.

Steroids. LXVIII.[1] 17-Ethylepitestosterone

BY E. BATRES, G. ROSENKRANZ AND FRANZ SONDHEIMER

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In view of the facile preparation of 17-methylepitestosterone from 17-methylene-Δ^4-androsten-3-one through preferential epoxidation of the exocyclic double bond, followed by lithium aluminum hydride reduction and manganese dioxide oxidation,[1] we decided to prepare the hitherto unknown 17-ethylepitestosterone (IV) by an analogous route. This substance was required for testing for possible ana-

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[1] Paper LXVII, F. Sondheimer, O. Mancera, M. Urquiza and G. Rosenkranz, THIS JOURNAL, **77**, 4145 (1955).