pyridine and 100 ml. of acetic anhydride were added slowly, with stirring and slight cooling.

After several hours a clear solution, free of undissolved particles, resulted. After 20 hours at room temperature, the solution was added to a large volume of vigorously stirred ice and water and the dingy-looking precipitate was washed free of acid with water. A second acetylation treatment[1,8] resulted in no change in acetyl content or in intrinsic viscosity. To provide comparison with the results of others, several variations of this procedure are indicated in Table I.

For acetylation with pyridine as catalyst at 100°, 5 g. of oven-dried polysaccharide (60 mesh) was stirred for 3 hours with 20 ml. of pyridine and 17 ml. of acetic anhydride. The homogeneous solution was cooled, poured into vigorously agitated ethanol, and the colorless precipitate was washed free of acid and dried in the air.

For acetylation with fused sodium acetate as catalyst at 100°, 5 g. of air-dried corn amylose (60 mesh) was soaked in 75 ml. of acetic anhydride overnight, then 1.5 g. of fused sodium acetate was added and the mixture stirred at 100° for 6 hours. The homogeneous solution was cooled, poured into vigorously stirred ice-water, and the colorless product was washed free of acid with water.

Solubility of the Triacetates.—Corn amylose triacetates prepared by the formamide or sodium acetate methods were soluble in acetone; that prepared by the pyridine method at 100° was not. All corn amylose triacetate preparations, as well as the triacetates from corn starch, were soluble in chloroform and 1,1,2-trichloroethane. Preparations of waxy corn starch triacetate from both the pyridine method at 100° and the formamide method were soluble in acetone as well as in the chlorinated solvents. Corn amylopectin triacetate prepared by the pyridine method at 100° was insoluble in the chlorinated solvents, but that prepared by the formamide method was readily soluble.

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Alkylation of 2-Naphthol by Esters of Aliphatic Acids

BY SAUL PATAI AND M. BENTOV

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In the course of a study on the preparation of aromatic methacrylates[1] the transesterification of methyl methacrylate with 2-naphthol in the presence of sulfuric acid was investigated. Instead of the expected ester, 2-methoxynaphthalene was formed. In order to elucidate this reaction, the transesterification of other aliphatic esters with other phenolic compounds was tried, using sulfuric acid, orthophosphoric acid or metallic sodium as the catalyst. Phenol, 1-naphthol, 4-hydroxybiphenyl and 4-nitrophenol did not react with methyl methacrylate or ethyl acetate. 2-Naphthol, on the other hand, reacted readily in the presence of sulfuric acid, but not of phosphoric acid or sodium, with methyl methacrylate, methyl acetate, ethyl acetate and ethyl butyrate, yielding 2-methoxynaphthalene with the methyl esters and 2-ethoxynaphthalene with the ethyl esters, but failed to react with ethyl formate or dimethyl oxalate. With methyl benzoate the normal product of transesterification, 2-naphthyl benzoate, was obtained.[2]

2-Naphthol is known to be one of the very few phenols which can be alkylated by alcohols in the presence of acids.[3] This fact may be related to the tautomerizability of 2-naphthol.[4]

As, however, our experiments were carried out under strictly anhydrous conditions, no alcohol could be formed as an intermediate in the reaction. It must, therefore, be assumed, that the alkylation is caused in both cases by the hydrogen alkyl sulfate, formed in the conditions of our experiments from the ester and sulfuric acid. The dissociation constant of formic acid is about ten times, and that of oxalic acid about a thousand times greater than that of either acetic, butyric or methacrylic acid: the failure of the reaction with the esters of formic and oxalic acid could then be due to the strength of these acids, which prevents the formation of the alkylsulfuric acids by interaction of the esters with sulfuric acid.

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Experimental

A mixture of 0.04 mole of 2-naphthol, 0.1 ml. of concencentrated sulfuric acid and 0.08 mole of the ester was refluxed for four hours with the exclusion of moisture. (In the case of methyl methacrylate, some hydroquinone was added to the reaction mixture.) The product was poured into an excess of 5% aqueous sodium hydroxide solution and cooled for one hour in an ice-bath, and the resulting precipitate filtered and recrystallized from ethanol. 2-Methoxy- and 2-ethoxynaphthalene were identified by melting point (72 and 37°, respectively) and mixed melting point with authentic samples. Yield of 2-methoxynaphthalene from methyl acetate 20–25%; from methyl methacrylate 45–50%; of 2-ethoxynaphthalene from ethyl acetate 40–45%; from ethyl butyrate 20–25%.

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[1] S. Patai, M. Bentov and M. E. Reichmann, THIS JOURNAL, **74**, 845 (1952).

[2] C. A. Bischoff and A. Hedenstrom (*Ber.*, **35**, 3449 (1902)) obtained di-2-naphthyl oxalate from diphenyl oxalate and 2-naphthol, and report the failure of the reaction with diethyl oxalate.

[3] C. Liebermann and A. Hagen, *ibid.*, **15**, 1427 (1882); L. Gattermann, *Ann.*, **244**, 72 (1888); W. A. Davis, *J. Chem. Soc.*, **77**, 33 (1900); L. F. Fieser and W. C. Lothrop, THIS JOURNAL, **57**, 1459 (1935).

[4] N. N. Voroshcov, *Bull. Inst. Polyt. Ivanovo-Voznesensk*, **6**, 125 (1922); *C. A.*, **17**, 1637 (1923); J. C. Salfeld, *Ber.*, **73**, 376 (1940).

Cohumulone, a New Hop Constituent

BY F. L. RIGBY AND J. L. BETHUNE

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In the course of an investigation to develop a quantitative method for the estimation of the isohumulone content of beer, petroleum ether extracts of several beers were distributed in a 100-tube all-glass countercurrent apparatus using a solvent system of 2,2,4-trimethylpentane and a phosphate–citrate buffer *p*H 4.9. The concentration in each tube was established by dissolving an aliquot of the upper phase in alkaline methanol and reading the optical density at 255 mμ. Figure 1 shows the distribution pattern for a typical extract after 100 transfers. Two major constituents and at least one minor constituent are present with partition ratios of 0.9, 1.9 and 3.2. In addition, the tubes at each extremity of the distribution train contain mixtures of unidentified substances. A sample of pure humulone (*o*-phenylenediamine complex, m.p. 117°), after conversion to isohumulone either by the method of Windisch, *et al.*,[1] or by boiling in aqueous phosphate buffer of *p*H 5.2, yields a product conforming to the properties of isohumulone and also having a partition ratio of 1.9 when distributed using this solvent system. A search for the origin of the substance showing maximum concentration in tube 47 and a partition ratio of 0.92 revealed that this substance did not arise from lupulone, soft resins, hard resins or humulinone but was produced, together with isohumulone, by boiling the lead salt salt fraction of a hop extract.

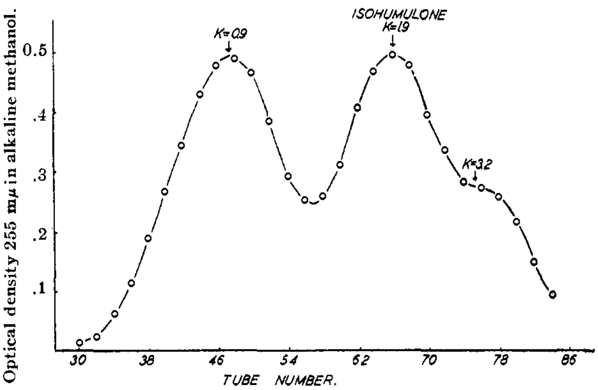

Fig. 1.—Distribution pattern for a beer extract: $n = 100$; solvent system, 2,2,4-trimethylpentane and phosphate-citrate buffer *p*H 4.9.

It was necessary therefore as a result of these observations to make a critical study of the lead salt fraction. Figure 2 shows the distribution pattern for the lead salt fraction of 1951 B. C. Bullion hops after 65 transfers using the system 2,2,4-trimethylpentane–phosphate buffer *p*H 8.5. The substance showing maximum concentration in tube 22 and a partition ratio of 0.53 is believed to be a new constituent of hops and has been assigned the name *cohumulone.* This substance was purified by repeated distributions using two solvent systems and high transfer numbers. The final product was a light-yellow oil at room temperature which formed a waxy solid on slight cooling. *Anal.* Calcd. for $C_{20}H_{32}O_5$: C, 69.23; H, 8.79; mol. wt., 364. Found: C, 69.1, 69.4, 69.4; H, 8.6, 8.8, 8.8; mol. wt. (by titration), 354. Cohumulone, like humulone, forms both a lead salt and an *o*-phenylenediamine complex but the solubility of the cohumulone product in each case is slightly greater than that of the humulone product. When boiled in phosphate buffer, *p*H 5.2, cohumulone is transformed to the new bitter substance of beer.

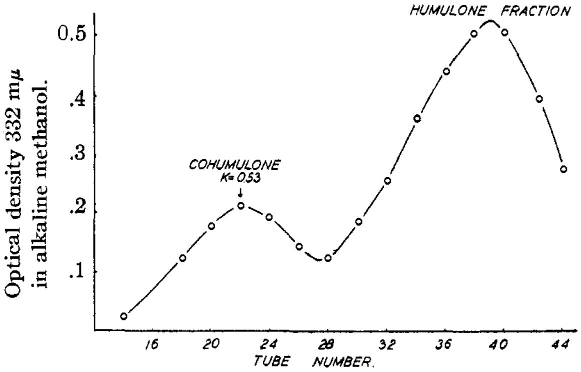

Fig. 2.—Distribution pattern for the lead salt fraction of a hop extract: $n = 65$; solvent system, 2,2,4-trimethylpentane and phosphate buffer *p*H 8.5; optical density units, mμ.

Cook and Harris[2] have reported the presence of humulinone in the lead salt fraction of Kent Golding and Worcester Fuggle hops. In the present investigation humulinone has been isolated from several varieties of Canadian and American hops. Purified humulinone from these sources distributes with a partition ratio of approximately 1 in a system of 2,2,4-trimethylpentane and 0.5 *M* monosodium phosphate adjusted to *p*H 3.2 with phosphoric acid. No humulinone, however, can be detected in these hops by distribution of either the lead salt fractions or the complete extracts. This evidence is supported by infrared and ultraviolet absorption spectra of humulinone, humulone and the lead salt fraction and permits us to conclude only that humulinone is not a natural constituent of hops but is an artifact in the method of isolation.

The second maximum in the distribution pattern, Fig. 2, is due predominantly to humulone but a theoretical curve for one substance cannot be fitted to this portion of the pattern. It is apparent, therefore, that a third component is present in the lead–salt fraction and it may be possible to accomplish its isolation by the use of a larger number of transfers or another solvent system.

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(1) W. Windisch, P. Kolbach and R. Schleicher, *Wochschr. Brau.*, **44**, 453, 473, 485, 497 (1927).

(2) A. H. Cook and G. Harris, *J. Chem. Soc.*, 1873 (1950).

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Derivatives of *o*-, *m*-, and *p*-Aminobenzotrifluoride. II. Azomethines Containing the Trifluoromethyl Group[1]

By Paul M. Maginnity and John L. Eisenmann

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A previous paper in this series[2] describes the preparation of a number of derivatives of the isomeric aminobenzotrifluorides, especially heterocyclic compounds. In conjunction with a study of certain azomethines being carried out in this Laboratory,[3] it was found desirable to prepare at

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(1) Parts of this paper were taken from a thesis submitted by John L. Eisenmann to the Graduate School of Boston College in partial fulfillment of the requirements for the degree of Master of Science.

(2) P. M. Maginnity and C. A. Gaulin, This Journal, **73**, 3579 (1951).

(3) *Cf.* P. M. Maginnity and T. J. Gair, *ibid.*, **74**, 4958 (1952).