NOTES.

Glucovanillin and a Colour Reaction for Vanillin. By WILLIAM V. THORPE and R. TECWYN WILLIAMS.

HELFERICH and SCHMITZ-HILLEBRECHT (*Ber.*, **1933**, **66**, 378) have shown (and we have confirmed) that, whereas phenyl-β-glucoside can be prepared by condensing phenol with β-penta-acetyl glucose in the presence of *p*-toluenesulphonic acid, phenyl-α-glucoside results if anhydrous zinc chloride is used as catalyst. When this method was applied to prepare the vanillin glucosides, with either catalyst, the only crystalline product isolated was tetra-acetyl vanillin-β-glucoside. The procedure used by Helferich and Schmitz-Hillebrecht was followed exactly in both cases, vanillin being used instead of phenol. The tetra-acetyl vanillin-β-glucoside (cf. Fischer and Raske, *Ber.*, 1909, **42**, 1465), recrystallised from aqueous alcohol, had m. p. 142—143°, $[\alpha]_D$ − 48·3° (*c* = 1 in chloroform) (Found: OMe, 6·5. Calc. for $C_{22}H_{26}O_{12}$: OMe, 6·4%). The 2 : 4-*dinitrophenylhydrazone* crystallised from pyridine–ligroin in orange needles, m. p. 202—203° (Found: OMe, 4·7. $C_{28}H_{30}O_{15}N_4$ requires OMe, 4·7%).

The tetra-acetate was deacetylated by sodium methoxide in methyl alcohol (cf. Bergmann and Heimhold, J., 1936, 505); the resulting vanillin-β-glucoside (β-glucovanillin) (Fischer and Raske, *loc. cit.*), recrystallised from methyl alcohol, formed long, very fine needles, m. p. 189—190°, $[\alpha]_D^{21°}$ − 86·6° (*c* = 0·72 in water) (Found: OMe, 10·1. Calc. for $C_{14}H_{18}O_8$: OMe, 9·9%). The 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan–ligroin in rust-red needles, m. p. 260—264° (Found: OMe, 6·0. $C_{20}H_{22}O_{11}N_4$ requires OMe, 6·3%).

Colour Reaction of Vanillin.—When 1 c.c. of an aqueous solution of vanillin is boiled with two drops of Millon's reagent, a characteristic stable purple colour (or precipitate with concentrated solutions) is obtained. The reaction seems specific for the vanillin group in that, out of 63 phenols examined (including eugenol, *iso*eugenol, guaiacol, and protocatechuic aldehyde and acid), only vanillin and vanillic acid gave the colour immediately. The reaction is given after longer boiling by acetylvanillin, β-glucovanillin, and potassium glucurovanillate. *iso*Eugenol with *excess* of reagent gives a fugitive purple colour turning to brown. *p*-Aminophenol gives a very transient purple turning to deep red.

The reaction is positive with a 0·002% vanillin solution. In very dilute solutions the mixture must stand for a few minutes to develop the maximum colour. With an excess of reagent, as with other phenols, no colour is obtained. 5-Nitrovanillin gives no reaction (cf. *o*-, *m*-, and *p*-nitrophenols and picric acid, which give no colour with Millon's reagent). The reaction is not given with the separated or paired constituents of Millon's reagent.—UNIVERSITY OF BIRMINGHAM. [*Received, December 10th*, 1936.]

Some Pyrimidine Derivatives. By A. BOWMAN.

THE following new pyrimidine derivatives were prepared by adaptations of known methods during an investigation which was not pursued owing to the appearance of publications (Bergel and Todd, *Nature*, 1936, **138**, 76, 406; Williams and Cline, *J. Amer. Chem. Soc.*, 1936, **58**, 1504), dealing in part with the same topics.

2 : 4 : 6-*Trimethylpyrimidine Dihydrate.*—Acetylacetone (11 g.) was added to a solution of acetamidine hydrochloride (10 g.) ("Organic Syntheses," VIII, 1) and potassium carbonate (28 g.) in water (95 c.c.). After 2—3 weeks the crystalline mass was collected, washed with a little cold water, and dried; evaporation of the mother-liquor gave a further crop (total yield, 3·8 g.). The *compound* separated from water or ether in long, colourless, filiform needles, m. p. 47—48°; it sublimed unchanged in a vacuum at 30—40° and had a strong odour of crude acetamide (Found: C, 53·0; H, 8·7; N, 17·4. $C_7H_{10}N_2,2H_2O$ requires C, 53·1; H, 8·9; N, 17·7%). Dehydration took place above the m. p.

2 : 4 : 6-*Trimethylpyrimidine.*—From the mother-liquor of the above preparation, saturated with potassium carbonate, ether extracted a yellowish oil (1 g.), b. p. 160° (approx.), which absorbed moisture from the air and solidified to crystals of the dihydrate. Aqueous solutions of both the base and the dihydrate yielded with mercuric chloride a sparingly soluble double *compound*, m. p. 169° after sintering at 164° (Found: Cl, 21·2. $C_7H_{10}N_2,2HgCl_2$ requires Cl, 21·3%).

2 : 4 : 6-*Tristyrylpyrimidine.*—2 : 4 : 6-Trimethylpyrimidine dihydrate (0·8 g.) was heated for 3—4 hours at 150° with an excess of benzaldehyde (4 g.) and a trace of anhydrous zinc

chloride. Excess of benzaldehyde was removed by steam-distillation and the residual brown solid was washed successively with water, alcohol, and a little cold benzene, and then dried (yield, 1·4 g.). The *compound* crystallised in microscopic colourless needles from benzene and was faintly yellow in bulk; m. p. 198—199° (Found : C, 87·1; H, 5·8; N, 7·2. $C_{28}H_{22}N_2$ requires C, 87·0; H, 5·7; N, 7·2%).

2-*Phenylpyrimidine*-4 : 6-*dicarboxylic Acid.*—2-Phenyl-4 : 6-dimethylpyrimidine (3 g.) (Pinner, *Ber.*, 1893, **26**, 2125) was heated for 12 hours under reflux with 1% potassium permanganate solution (1050 c.c.). The filtered solution after evaporation to small bulk (75 c.c.) was acidified with dilute hydrochloric acid and the precipitated white crystalline powder was collected, recrystallised from aqueous alcohol, and dried at 110°. The *acid* began to decompose at 165° and subsequently melted at a temperature depending on the rate of heating (Found : C, 59·1; H, 3·5; N, 11·5. $C_{12}H_8O_4N_2$ requires C, 59·0; H, 3·3; N, 11·5%).

2-*Phenyl*-4-*methylpyrimidine*-6-*carboxylic Acid.*—Oxidation of 2-phenyl-4 : 6-dimethylpyrimidine (5·5 g.) in boiling water (500 c.c.) by dropwise addition of aqueous potassium permanganate (9·5 g. in 500 c.c.) and fractional acidification of the concentrated filtrate from the reaction gave, in addition to the dibasic acid described above, the monobasic *acid* (0·7 g.), m.p. 112° (decomp.) (Found : C, 67·1; H, 4·9. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7%). Unchanged initial material (2·7 g.) was recovered.

2 : 4-*Dichloro*-5-*chloromethyl*-6-*methylpyrimidine.*—4-Methyl-5-hydroxymethyluracil (8 g.) (Kircher, *Annalen*, 1911, **385**, 293) and phosphorus oxychloride (80 c.c.) were heated on the water-bath for 8 hours. After removal of the excess of phosphorus oxychloride in a vacuum the residual oil was poured on ice; it solidified on standing. The yellowish-white solid was dissolved in a little alcohol and reprecipitated from the filtered solution by water (yield, 7·6 g.; 70%). The compound separated from light petroleum in large colourless prisms, m. p. 38—39° (Found : C, 34·1; H, 2·3; N, 13·3; Cl, 50·2. Calc. for $C_6H_5N_2Cl_3$: C, 34·0; H, 2·4; N, 13·2; Cl, 50·4%). Todd *et al.* (J., 1936, 1604) obtained a 37% yield and record m. p. 38—39°.

3-(2′ : 4′-*Dichloro*-6′-*methylpyrimidyl*-5′-*methyl*)-5-β-*hydroxyethyl*-4-*methylthiazolium Chloride.*—5-β-Hydroxyethyl-4-methylthiazole (104 mg.) (Buchman, *J. Amer. Chem. Soc.*, 1936, **58**, 1803) was heated for 24 hours at 60—65° with 2 : 4-dichloro-5-chloromethyl-6-methylpyrimidine (154 mg.) and absolute methyl alcohol (0·05 c.c.). The cooled product, washed with a little cold absolute alcohol and recrystallised by addition of ether to a warm solution in absolute alcohol (yield, 48 mg.), formed irregular, faintly yellow plates, m. p. 202·5° after sintering at 201° (Found : C, 41·2; H, 4·3; N, 11·9; Cl, 30·0. $C_{12}H_{14}ON_3Cl_3S$ requires C, 40·6; H, 4·0; N, 11·9; Cl, 30·0%). The *chloride* showed in alcoholic solution a blue fluorescence in ultraviolet light, and gave a positive formaldehyde-azo test (Kinnersley and Peters, *Biochem. J.*, 1934, **28**, 667). By the catatorulin test (Passmore, Peters, and Sinclair, *ibid.*, 1933, **27**, 842; Peters, *ibid.*, 1935, **29**, 712) no aneurin activity was shown.

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