NOTES.

The Measurement of Glass Electrode Potentials by a Valve Electrometer. By GUY DRUMMOND GREVILLE and NOEL FRANCIS MACLAGAN.

A VALVE electrometer was recently described by us (*Trans. Faraday Soc.*, 1931, **27**, 210) in which, by the application of a more sensitive galvanometer and a special switch, the accuracy of the apparatus of Harrison (J., 1930, 1528) was increased from ± 1 millivolt to ± 0·05 millivolt. Morton, commenting on this (J., 1931, 2977), remarks : " It is noteworthy, however, that the maximum deflexion which they obtained for a potential of 0·05 millivolt was only 0·6 mm., whereas the zero drift amounted to 2 mm. per minute." We must, however, point out that with our electrometer, readings are taken so rapidly (in about 3 seconds) that this zero drift is negligible. Thus, the following two series of successive measurements of the potential of a MacInnes and Dole type glass electrode were taken by two different observers :

82·84, 82·90, 82·91, 82·89, 82·85, 82·90 : mean = 82·88 mv.
Maximum positive error : + 0·03 mv.
„ negative „ − 0·04 mv.
82·88, 82·84, 82·89, 82·91, 82·92, 82·90 : mean = 82·89 mv.
Maximum positive error : + 0·03 mv.
„ negative „ − 0·05 mv.
Drift = 2 mm. in 50 seconds.

It is thus clear that an accuracy of ± 0·05 mv. is readily obtained with our simple apparatus.—COURTAULD INSTITUTE OF BIOCHEMISTRY, MIDDLESEX HOSPITAL, LONDON, W. 1. [*Received, December* 17*th*, 1931.]

The Composition of Salinigrin. A Correction. By HOOPER ALBERT DICKINSON JOWETT.

IN 1900 (J., **77**, 707) the author isolated from a sample of bark purchased as black willow, the botanical source of which was unknown, a glucoside different from salicin and named it " salinigrin " with regard to its source. The aglucone obtained from this glucoside agreed in certain respects with *m*-hydroxybenzaldehyde and, although the melting point of the mixed aglucone and synthetic aldehyde was not determined, it was described as the glucoside of *m*-hydroxybenzaldehyde, a new substance.

In 1902, Jowett and Potter (*Y. Book Pharm.*, 1902, 483), as a result of the examination of 31 authentic specimens of varieties of European and American willow and poplar barks, found this glucoside to occur in only one species, namely, *S. discolor*, Muhl, and not in *S. nigra*, Marsh.

Recently Bridel and Rabaté (*J. Pharm. Chim.*, 1930, **11**, 561) isolated from a bark, described as black willow from N. America, a glucoside having similar physical constants to the salinigrin described above, but from their examination of it they concluded it to be identical with picéoside—a glucoside isolated by Tanret from *Picea excelsa*, Link, and by Charaux and Rabaté from *Amelanchier vulgaris*, Moench. This substance is the glucoside of *p*-hydroxyacetophenone.

Samples of the original glucoside and of the aglucone isolated from it being available, determinations of the melting points of mixtures of the aglucone with both *m*-hydroxybenzaldehyde and *p*-hydroxyacetophenone were made. Both the original aglucone and that recently prepared melted at 109°. A specimen of synthetic *m*-hydroxybenzaldehyde, m. p. 104—105°, melted at 70° when mixed with the aglucone. A specimen of synthetic *p*-hydroxyacetophenone melted at 108—109°, alone or mixed with the aglucone.

The author therefore confirms the statement that the glucoside found in the bark of *S. discolor*, Muhl, and named salinigrin is identical with the picéoside of Tanret and is the glucoside, not of *m*-hydroxybenzaldehyde, but of *p*-hydroxyacetophenone.—WELLCOME CHEMICAL WORKS, DARTFORD. [*Received, January 20th*, 1932.]

The Reduction of l-n-*Butylvinylcarbinol to Ethyl*-n-*butylcarbinol. A Correction.* By ROBERT IAN JOHNSON and JOSEPH KENYON.

IT was stated by Kenyon and Snellgrove (J., 1925, **127**, 1169) that when *l*-*n*-butylvinylcarbinol is reduced by hydrogen in the presence of colloidal platinum the resulting ethyl-*n*-butylcarbinol is lævorotatory. This experiment was repeated by Levene and Haller (*J. Biol. Chem.*, 1929, **83**, 579), who found that the resulting ethyl-*n*-butylcarbinol, although possessing the same magnitude of rotatory power as that obtained by Kenyon and Snellgrove (*loc. cit.*), was dextrorotatory. We have accordingly repeated the work and have confirmed the result obtained by Levene and Haller.

A specimen of *dl*-*n*-butylvinylcarbinyl hydrogen phthalate prepared by Kenyon and Snellgrove (*loc. cit.*) was converted into the strychnine salt, which was crystallised ten times from ethyl alcohol. The *l*-*n*-butylvinylcarbinyl hydrogen phthalate obtained by the decomposition of this salt had $[\alpha]_D^{20^\circ} - 12{\cdot}8^\circ$ ($c = 5{\cdot}0$, $l = 2{\cdot}0$) in ethyl-alcoholic solution; on hydrolysis it yielded *l*-*n*-butylvinylcarbinol, b. p. 83°/35 mm., $\alpha_{5461}^{20^\circ} - 6{\cdot}27^\circ$ ($l = 0{\cdot}25$), $n_D^{20^\circ}$ 1·4340, which decolorised bromine solution rapidly.

l-*n*-Butylvinylcarbinol (3·4 g.) in dry ether was reduced by hydrogen at an excess pressure of one atmosphere in the presence of platinum oxide (Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397), and the theoretical quantity of hydrogen was absorbed in about 4 hours. The ethereal solution was filtered and kept over potassium carbonate; the ether was removed, and the ethyl-*n*-butylcarbinol distilled ; b. p. 64—65°/16—17 mm., $n_D^{20^\circ}$ 1·4202, $\alpha_{5461}^{20^\circ} + 1{\cdot}82^\circ$, $\alpha_D^{20^\circ} + 1{\cdot}53^\circ$ ($l = 0{\cdot}25$).

This carbinol, which did not decolorise bromine solution, was converted into its hydrogen phthalic ester which, after crystallisation from light petroleum, had $[\alpha]_D^{20^\circ} + 19{\cdot}3^\circ$ ($c = 5{\cdot}0$, $l = 2$) in ethyl-alcoholic solution and m. p. 48° alone and when mixed with the hydrogen phthalic ester of *d*-ethyl-*n*-butylcarbinol obtained by the resolution of *dl*-ethyl-*n*-butylcarbinol (Pickard and Kenyon, J., 1913, **103**, 1923).—BATTERSEA POLYTECHNIC, S.W. 11. [*Received, December 19th*, 1931.]

The Preparation of Quinoline-2-aldehyde and Some of its Derivatives.

By KENNETH ERNEST COOPER and JULIUS BEREND COHEN.

THE preparation of this aldehyde by Miller and Spady's method (*Ber.*, 1885, **18**, 3237, 3404) gives a very poor yield (10%) of impure material which is difficult to crystallise. The following modification enables the material to be obtained in a practically pure, easily crystallisable form in a yield exceeding 50% of the theoretical.

An aqueous solution of 30 g. of crystalline sodium carbonate containing 30 g. of quinoline-2-acrylic acid is made up to 400 c.c., covered with ether (*ca.* 1 l.), and cooled in tap water while a solution of 50 g. of potassium permanganate in the minimum quantity of water (about 800 c.c.) is added during 1 hour with constant shaking. After ½ hour, the liquid is filtered, and the aqueous layer extracted once more with ether. The combined ethereal extracts are dried over sodium sulphate and evaporated. Yield, 12 g. of aldehyde, m. p. 67—69°. The product crystallises in colourless rhombic crystals from light petroleum.

6-*Acetamido*-2-(2'-*quinolylstyryl*)*quinoline methochloride*, m. p. 278° (decomp.), crystallised in golden-yellow needles from 70% alcohol (Found: Cl, 9·3. $C_{23}H_{20}ON_3Cl$ requires Cl, 9·1%). It was obtained by 2 hours' boiling of an alcoholic solution of 6-acetamidoquinaldine methochloride with the theoretical amount of quinoline-2-aldehyde and a trace of piperidine.

Hydrolysis of the acetyl compound with boiling hydrochloric acid for ½ hour, followed by neutralisation with ammonia and crystallisation from aqueous alcohol, gave 6-*amino*-2-(2'-*quinolylstyryl*)*quinoline methochloride* in bright red needles, m. p. 262° (decomp.) (Found: Cl, 10·0. $C_{21}H_{18}N_3Cl$ requires Cl, 10·2%).

Quinoline-2-*aldehyde* p-*hydroxyanil*, $C_9H_6N{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}OH$, melts at 240—241° to a red liquid. It crystallised in bright yellow plates (Found: N,11·8. $C_{16}H_{12}ON_2$ requires N, 11·3%), and was obtained by melting a mixture of the aldehyde and the theoretical quantity of *p*-aminophenol on the water-bath until solidification occurred.

The p-*dimethylaminoanil*, m. p. 148—150°, crystallised in golden-yellow needles from methyl alcohol (Found: N, 15·5. $C_{18}H_{17}N_3$ requires N, 15·3%). It was obtained in a similar way to the *p*-hydroxy-compound from dimethyl-*p*-phenylenediamine. A colourless deliquescent *dihydrochloride* was precipitated from ethereal solution by dry hydrogen chloride (Found: Cl, by titration, 21·0. $C_{18}H_{17}N_3,2HCl$ requires Cl, 20·4%).

The p-*diethylaminomethylanil* was obtained by heating theoretical quantities of the aldehyde and *p*-aminobenzyldiethylamine for 5 minutes on the water-bath and then keeping the mixture at room temperature over-night. The solid was washed with light petroleum and recrystallised from that solvent, forming pale yellow plates, m. p. 44—46° (Found : N, 13·9. $C_{21}H_{23}N_3$ requires N, 13·5%).

This paper forms the unpublished part of a research carried out with the support of the Medical Research Council.—THE MEDICAL SCHOOL, LEEDS. [*Received, January 13th*, 1932.]

The Preparation of Dibromofluorescein. By MONTAGUE ALEXANDER PHILLIPS.

BAYER prepared " dibromofluorescein " in 1876 (*Annalen*, **183**, 38) by the action of bromine on fluorescein, but it is doubtful whether his preparation, or indeed any preparation made by this method in the presence of solvents, was pure. Pure dibromofluorescein (m. p. 280—290°) was first mentioned by Orndorff and Hemmers (*J. Amer. Chem. Soc.*, 1927, **49**, 1277); presumably they obtained it by fractional crystallisation and hydrolysis of the dibenzoate.

Although these authors refer to hydrochlorides of fluorescein derivatives, there is no hint that similarly constituted hydrobromide compounds are formed in the bromination of fluorescein.

It has been found that this bromination leads to variable mixtures of dibromofluorescein hydrobromide and fluorescein, from which the combined hydrogen bromide can be quantitatively removed by hot water or cold caustic alkali. When bromination was conducted in glacial acetic acid, pure dibromofluorescein hydrobromide could not be obtained; the use of 80% acetic acid as solvent gave, however, an 85—88% yield of this substance, from which, by the action of hot water, pure dibromofluorescein, m. p. 285°, was obtained. Since this compound, without further purification, gave a 95% yield of pure diacetate, it must be concluded that little or no eosin is formed during the reaction.

Bromination of Fluorescein.—(a) *With* 1·6 *mols. of bromine.* To a suspension of fluorescein (66 g.) in glacial acetic acid (250 c.c.) was added at 80° a solution of bromine (50 g.) in glacial acetic acid (200 c.c.). After 2 hours' stirring at the same temperature, the product was collected and washed with alcohol and ether. Dried at 90°, it weighed 91 g. and contained 34·2% of bromine. Washing with hot water removed 12·2% of bromine as hydrobromic acid and left 80 g. of material, m. p. 250° (Br, 25·3%); this corresponds to a mixture of 77·5% of dibromofluorescein and 22·5% of fluorescein.

(b) *With* 2·0 *mols. of bromine.* The above experiment was repeated, 2 mols. of bromine (64 g.) being used; the yield was 96 g. (Br, 37·0%). This lost 13% of its weight on treatment with hot water or by reprecipitation of its alkaline solution with acetic acid.

The mixture of dibromofluorescein (89%) and fluorescein (11%) obtained in this way, m. p. 250—255°, contained 29·0% of bromine.

(c) *With* 2·5 *mols. of bromine.* This gave a yield of 100 g. (Br, 39·2%) which lost 12 g. on treatment with hot water or cold caustic alkali. The mixture obtained, m. p. 255°, consisted of 94% of dibromofluorescein and 6% of fluorescein (Br, 30·6%).

(d) *With* 80% *acetic acid as solvent.* A repetition of (b) with 80% instead of glacial acetic acid gave a yield of 100 g. (Found: Br, 41·5. Calc. for $C_{20}H_{10}O_5Br_2,HBr$: Br, 42·0%). This lost 14·0% of hydrogen bromide when treated with hot water (calc., 14·0%) and gave pure dibromofluorescein, m. p. 285° (Found: Br, 32·7. Calc.: Br, 32·7%). It is a deep red, microcrystalline powder, which crystallises from 30% alcohol in red plates. It is soluble in alkalis to a deep red solution; unlike Bayer's "dibromofluorescein," it dissolves in sodium carbonate solution without evolution of carbon dioxide.

Dibromofluorescein Diacetate.—Dibromofluorescein (10 g.), mixed with acetic anhydride (40 c.c.) and one drop of sulphuric acid, was refluxed for one hour; when the mixture was poured into water the diacetate, m. p. 210°, was precipitated in 95% yield (Found in crude material: Br, 27·9; CH_3·CO, 14·8. Calc.: Br, 27·9; CH_3·CO, 15·0%). Recrystallised from acetic anhydride or nitrobenzene, it consisted of colourless or pale yellow plates, m. p. 211°. Hydrolysis with alcoholic sulphuric acid gave a quantitative return of pure dibromofluorescein, m. p. 285°.—RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LIMITED, LONDON, S.W. 18. [*Received, December* 12*th*, 1931.]