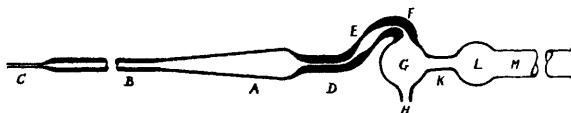


## NOTES.

*A New Pipette.* By H. NORMAN RIDYARD.

THIS pipette combines the essential principle of that of Jakowkin (*Z. physikal. Chem.*, 1899, **29**, 626) with some features of the pyknometer, and was designed for the accurate delivery of small volumes of bromine-benzene solutions.

FIG. 1.



A gently tapering bulb, *A*, is joined at the lower end to a stem of capillary tubing ( $1-1\frac{1}{2}$  mm.), *B*, which is drawn out at the lower end to a jet, *C*, of very fine bore. The upper end of *A* merges into a very fine capillary, *D*, which bends and expands, as shown, into the small bulb *E*, contracts into the capillary *F*, slightly wider than *D*, and finally enters the bulb *G* (2 cm. diam.). The portion from the junction with *B* to the end of *H* is drawn in one piece

from glass tubing wider than *A*, as joints impede draining. The external diameter of *D*, *E*, *F*, should be over 8 mm. to reduce risk of breakage. The optimum sizes of the capillaries at *C* and *D* vary with the viscosity of the liquid to be used. The upper portion of the pipette may be a straight tube, or of the form *K*, *L*, *M*, which can be packed with glass wool and soda-lime, etc.

The pipette is filled by suction, facilitated by a piece of rubber tubing, *H* being closed by a finger. When *G* is half full, thus receiving all liquid which may have changed in concentration, the pipette is turned with *H* downward, liquid in *G* blown out, and the level of liquid adjusted to the middle of *D* by applying filter-paper to *C*. The contents may then be blown out.

Two pipettes (1.7 c.c., 2.3 c.c.) were examined by weighing seven deliveries. Errors did not exceed  $\pm 0.02\%$  with water, or  $\pm 0.1\%$  with benzene. The pipettes delivered 0.1—0.2% more benzene than water under similar conditions.

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*A Reaction of Caryophyllene.* By DAVID T. GIBSON.

THE fact that Deussen (*J. pr. Chem.*, 1927, **117**, 282) has just published the results of an investigation on the extension of Buchner's reaction (*Ber.*, 1913, **46**, 2680) to caryophyllene makes it desirable to describe a reaction of that sesquiterpene which was discovered in the course of a similar study, and was to have been included in a subsequent publication.

When a solution of diazoacetic ester in caryophyllene (b. p.  $124^\circ/12$  mm.,  $n_D^{20}$  1.5012) is gradually added to an excess of caryophyllene at  $180$ — $200^\circ$  in presence of finely divided copper, a cyclopropane ester (compare Deussen, *loc. cit.*), b. p.  $130$ — $160^\circ/2$  mm., can easily be separated from the excess of the hydrocarbon. This ester is not derived from a casual impurity, for the recovered caryophyllene continues to give as good a yield on repeated treatment. The ester is hydrolysed by 10% alcoholic potash, the alcohol and any uncombined oil are distilled in steam, and the potassium salt decomposed with acid. The crude cyclopropane acid may readily be crystallised from ligroin, benzene, or acetic acid; it has m. p.  $165^\circ$ , and  $[\alpha]_{5461} - 40^\circ$  in alcohol ( $c = 1$ ) (Found: C, 77.4; H, 9.7; equiv., 248; *M*, in camphor, 268.  $C_{16}H_{25}CO_2H$  requires C, 77.8; H, 10.0%; *M*, 262). The acid is stable to bromine

in chloroform, and is only very slowly attacked by boiling acid permanganate. The mother-liquor from its crystallisation contains a resinous acid, which is the sole product when more concentrated alkali is used in the hydrolysis.

This test was applied to the fraction of supa oil which Henderson, M'Nab, and Robertson (J., 1926, 3077) had shown to consist largely of copæne. Ethyl diazoacetate (20 g.) in supa oil (120 c.c.) was added drop by drop to supa oil (80 c.c.) at 165° in presence of copper. 165 C.c. of supa oil were recovered unchanged, and after the usual treatment, 1.5 g. of the pure *cyclopropane* acid isolated; m. p. 165°, unaltered by admixture with a specimen prepared from caryophyllene. The presence of caryophyllene in that sample of supa oil was confirmed, though much less readily, by the preparation from it of Wallach's caryophyllene alcohol, m. p. 94°. No analogous acid was obtained from either cadinene or cedrene.—  
THE UNIVERSITY, GLASGOW. [Received, February 4th, 1928.]

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