rotenone, but only on the basis of a color test not specific for rotenone itself. Camson[3] has obtained a crystalline substance resembling rotenone from a carbon tetrachloride solution of the oil-free resin from the seeds.

Two kg. of ground yam bean seeds from Mexico were extracted with ether, the ether removed, and the insecticidally active resin (1.4%) separated from the large amount of fatty oil (26.7%) by partition between 90% acetic acid and petroleum ether. The oil-free resin in benzene solution was fractionated by chromatographic adsorption on alumina. The fraction giving a strong Goodhue[4] red color test deposited from benzene solution several crops of crystalline material giving little or no color test. The benzene was removed from the remaining solution, and the residue taken up in hot carbon tetrachloride. A heterogeneous brownish deposit formed after cooling overnight, and was removed. On scratching the flask walls or seeding with rotenone–carbon tetrachloride solvate, a mass of white needles was deposited, similar in appearance to the rotenone solvate. When warmed with alcohol, these needles were converted rapidly to thin plates like those of rotenone.

The compound was identified as rotenone by a m. p. of 164–165° (cor.) both alone and in admixture with known rotenone; the formation of a dehydro compound of m. p. 222°; optical rotation in 1% benzene solution $[\alpha]^{25}\text{D}$ −236°; quantitative Goodhue and Meyer and qualitative Durham color tests; and a high toxicity to insects; all in satisfactory agreement with the corresponding properties of authentic rotenone.

The isolated rotenone amounted to about 0.1% of the original beans. The total material giving the red color test in this sample was 0.15%, calculated as rotenone. It is therefore probable that rotenone itself accounts for a substantial proportion of the color tests reported by previous workers. Some samples have been reported to have a much higher content of color-producing material than the sample used in this work.

Rotenone does not account fully for either the toxicity or the red color test of the yam bean. A number of other compounds of yet unknown constitution also have been isolated, some giving the color test, and some showing definite toxicity to insects. Investigation of these compounds is now in progress.

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[3] E. J. Camson, Orbis Products Corp., Newark, N. J., personal communication.

[4] Goodhue, *J. Assoc. Off. Agr. Chem.*, **19**, 118 (1936).

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RECEIVED OCTOBER 11, 1943

## SYNTHESIS OF 1,4-EPOXYCYCLOHEXANE

*Sir:*

It was to be expected that refluxing 1,4-cyclohexanediol in the presence of activated alumina would yield cyclohexadienes and cyclohexanol.[1] It has now been found, however, that 1,4-epoxycyclohexane is predominantly formed. It has also been observed that by passing a solution of *trans*-1,4-cyclohexanediol over activated alumina at 275°, 73% of 1,4-epoxycyclohexane is formed, while the *cis* isomer under similar conditions gives only 28% of the epoxide. The type of solvent, contact agent, and temperature used exert a strong influence upon the yield of the epoxide.

1,4-Epoxycyclohexane boils at 120.1° (760 mm.), $d^{20}_4$ 0.9707, $n^{20}\text{D}$ 1.4477, $M^{20}\text{D}$ 27.05. *Anal.* Calcd. for $C_6H_{10}O$: C, 73.47; H, 10.20. Found: C, 74.19; H, 10.14. It is soluble in the usual organic solvents and is partially soluble in water, with which it forms an azeotropic mixture boiling at 90°. It is soluble in 40–60% sulfuric acid from which it may be recovered by dilution with water. On heating with 48% aqueous hydrogen bromide *trans*-1,4-dibromocyclohexane is formed.

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[1] V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The MacMillan Company, New York, 1936, p. 106.

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## A NEW POTENTIOMETRIC METHOD TO DETERMINE CATIONS AND ANIONS WITH COLLODION AND PROTAMINE-COLLODION "MEMBRANE ELECTRODES"

*Sir:*

I should like to point out that collodion membranes of high ionic selectivity as described recently[1] may be used successfully for the potentiometric determination of $K^+$, $Na^+$, $Li^+$, $NH_4^+$, $Mg^{++}$, and probably some other cations. The nature of the anion seems to have no specific influence. As yet, however, the collodion membranes are inferior to Marshall's[2] clay membranes in that the presence of other cations seriously interferes in all instances.

Collodion membranes impregnated with protamine[3] are electropositive, and show an analogous selectivity with regard to anions as do clay or collodion membranes with regard to cations. Such protamine collodion membranes may be used for the determination of $Cl^-$, $Br^-$, $I^-$, $F^-$, $ClO_3^-$, $ClO_4^-$, $BrO_3^-$, $IO_3^-$, $NO_3^-$, acetate$^-$, etc. For some of these ions no other potentiometric method is available.

The determinations may be made in various ways. The potential difference which arises between a known solution on the one side of the membrane and the solution of unknown concen-

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[1] K. Sollner, I. Abrams and C. W. Carr, *J. Gen. Physiol.*, **25**, 7 (1941); C. W. Carr, Ph.D. Thesis, University of Minnesota, 1942.

[2] C. E. Marshall and W. E. Bergman, THIS JOURNAL, **63**, 1911 (1941), *J. Phys. Chem.*, **46**, 52, 325 (1942); C. E. Marshall and C. A. Krinbill, THIS JOURNAL, **64**, 1814 (1942).

[3] I. Abrams, and K. Sollner, *J. Gen. Physiol.*, **26**, 369 (1943).

tration on the other side of the membrane may be evaluated on the basis of some semi-theoretical standard curve. Or, these potential values may be compared to an empirical curve, determined for a specific membrane in advance. A third method consists of an electrometric titration: the membrane separates the solution of unknown concentration from water, to which electrolyte solution of known (higher) concentration is added stepwise, whereby the potential difference is diminished stepwise and finally is reversed. Zero potential difference indicates that the activity of the critical ion is the same on both sides of the membrane. The preliminary results listed below were obtained using the third method.

TABLE I

THE DETERMINATION OF CATIONS WITH COLLODION MEMBRANES

| Electrolyte (0.01000 mole/liter) | Concentration, found, mole/liter |
|---|---|
| KCl | 0.00998 |
| $KClO_3$ | .00988 |
| $KClO_4$ | .01008 |
| $KNO_3$ | 01022 |
| $K_2SO_4$ | .01012 |
| NaCl | .01014 |
| LiCl | .01012 |
| $NH_4Cl$ | .01000 |
| $MgCl_2$ | .01018 |

TABLE II

THE DETERMINATION OF ANIONS WITH PROTAMINE COLLODION MEMBRANES

| Electrolyte (0.01000 mole/liter) | Concentration found mole/liter |
|---|---|
| KCl | 0.01016 |
| NaCl | .00980 |
| $MgCl_2$ | .01008 |
| NaF | .01012 |
| $KNO_3$ | .01016 |
| $NaNO_3$ | .00980 |
| NaAc | .01012 |
| $KClO_3$ | .01018 |
| $KClO_4$ | .00988 |
| $KIO_3$ | .01018 |

This method should be useful in studies of the activity of the counter-ions in colloidal systems, for the determination of the anion and cation binding capacity of proteins, and similar problems.

A detailed description and evaluation of this method will be published shortly. In how far "oil-chains" can be employed in a similar way for organic ions in general will also be discussed at a later date.

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RECEIVED OCTOBER 14, 1943

## X-RAY FIBER PATTERN FROM AMYLOSE WITH A GLYCEROL PLASTICIZER

*Sir:*

Reports from this Laboratory[1] have been made of films and fibers of amylose,[2] and a structure for the "B" modification of starch has been proposed on the basis of amylose film and fiber diagrams.[3] In the course of attempting to produce amylose fibers, plasticizers were employed to aid in the stretching of the amylose films. The X-ray fiber diagrams obtained from fibers containing plasticizers were by no means identical with those produced by fibers containing no plasticizer.[3]

In Fig. 1, a fiber diagram is reproduced of amylose with a glycerol plasticizer. The diagram was taken with Cu K $\alpha$ radiation and a sample to flat film distance of 3 cm. The fiber spacing is 7.5 Å. This is very different from the 10.6 Å. spacing found for the "B" modification of starch, and indicates a flexibility of the starch chain not found in the cellulose chain.

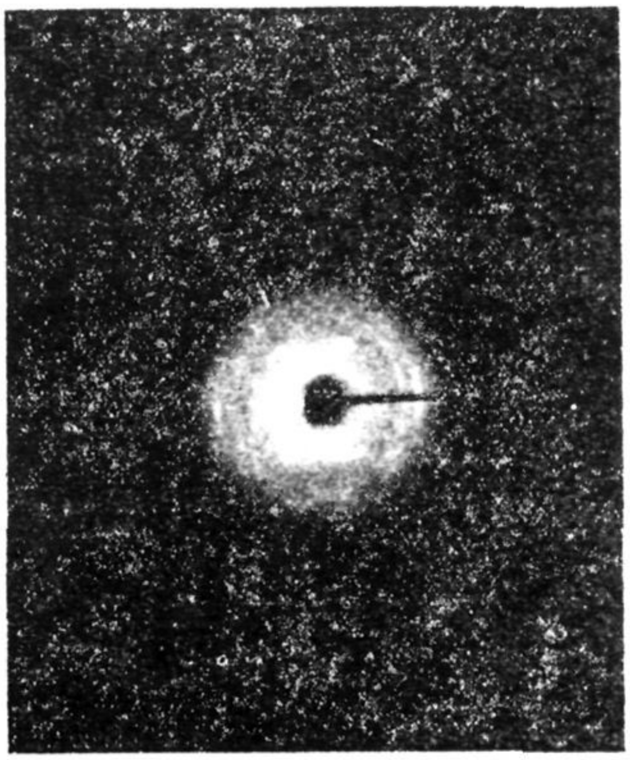

Fig. 1.—X-Ray fiber diagram of amylose with glycerol plasticizer. Fiber axis is vertical.

Alcohol-precipitated starch, the "V" modification, is found to have a helical structure and a periodicity along the helix of 8 Å.[4] The optical properties of this material indicate that the greatest polarizability is normal to the helix axis,[5,4] or normal to the long axis of the molecule. The greatest polarizability of the glycerol-amylose

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(1) R. Rundle and D. French, THIS JOURNAL, **65**, 558 (1943).

(2) The amylose used was prepared by T. Schoch's fractionation, *ibid.*, **64**, 2957 (1942). For a discussion of its purity and properties see L. Bates, D. French and R. Rundle, *ibid.*, **65**, 142 (1943).

(3) R. Rundle, L. Daasch and D. French, *ibid.*, in press.

(4) R. Rundle and D. French, *ibid.*, in press.

(5) R. Rundle and R. Baldwin, *ibid.*, **65**, 554 (1943).