

good yields as colorless crystals, possessing sharp melting points after recrystallization from light petroleum.

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COMMUNICATIONS TO THE EDITOR

CARROT LEAF CAROTENE

Sir:

We have isolated carotene from carrot leaves to determine whether it contains the components of carrot root carotene, or whether, like the majority of leaf carotenes reported, it is optically inactive. Only two optically active leaf carotenes, tea¹ and horse chestnut,² have been reported. The method of extraction described by Smith³ was followed with minor modifications. We obtained 0.370 g. of recrystallized carotene from 6 kg. of leaf powder.

Specific optical rotations and melting points were determined on two samples, one recrystallized from petroleum ether-ethanol, the other from *n*-heptane.

Sample	M. p., °C. (Berl block, corr.)	$[\alpha]_{D}^{25}$
Pet. ether-ethanol	175.7	+33.6° (36.6 mg. in 15 cc. benzene)
<i>n</i> -Heptane	176.8	+37.3° (33.0 mg. in 15 cc. benzene)

The specific rotation indicates approximately 10% of α -carotene.

The absorption spectrum in 95% ethanol was observed visually. Absorption maxima were found at 4533 Å. and approximately 4780 Å., nearly the positions of the maxima of β -carotene.

Adsorption on a column of Norit A (Pfanstiehl) from dichloromethane solution (method developed and shortly to be described by H. H. Strain) gave excellent resolution of the components. The first few drops of colored percolate, transferred to 95% ethanol, gave very sharp bands, with maxima at 4470 and 4738 Å., confirming the presence of α -carotene.

Adsorption on fibrous alumina from benzene and low boiling petroleum ether (50% by volume) showed the presence of a colored ring in the position to be expected for γ -carotene.⁴ This ring was extracted and re-adsorbed from fresh solvent on a new column. When re-extracted, the solution was too dilute for satisfactory spectroscopic identification. How-

(1) I. P. C. R. (Tokyo), **19**, 127 (1932).

(2) *Ber.*, **64**, 1349 (1931).

(3) J. H. C. Smith, *J. Biol. Chem.*, **96**, 35 (1932).

(4) *Ber.*, **66**, 407 (1933).

ever, the behavior of the ring is an indication of the presence of the γ -component.

It is concluded that carrot leaf carotene resembles carrot root carotene in its composition rather than the optically inactive carotenes hitherto found in most leaves.

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THE EFFECT OF THE SOLVENT ON THE POTENTIAL OF THE CHLORANIL ELECTRODE

Sir:

Since the original study of the chloranil electrode by Conant and Fieser,¹ it has been generally assumed both at Harvard and elsewhere² that "the potential of the saturated chloranil electrode against the hydrogen electrode is independent of the solvent (and has the value +0.664 volt at 25°)".³

This assumption is, of course, well founded provided the solution studied is really in equilibrium with the unsolvated solid chloranil and its hydroquinone. Since this electrode has been chiefly used in glacial acetic acid, the following observations seem important.

In the course of certain measurements in this solvent (to be published later) it appeared that if the value +0.664 volt was accepted for the chloranil electrode, all the potentials measured differed from those obtained in the same system when a hydrogen electrode was used. The discrepancy disappeared if the value +0.680 volt was assigned to the chloranil electrode. We therefore measured directly the effect of the solvent on the potential of cells without liquid junction and containing a hydrogen and a chloranil electrode, with the result that Conant and Fieser's value of +0.664 volt was confirmed in 50% aqueous alcohol, while in glacial acetic acid and in 50% aqueous dioxane the values +0.680 volt and +0.715 volt were obtained.

These differences are due to the fact—previously overlooked—that tetrachlorohydroquinone is solvated in certain solvents, as has indeed long been known.⁴ The solid phase in equilibrium with the saturated solution in glacial acetic acid is principally $C_6Cl_4(OH)_2 \cdot 2AcOH$, while in contact with dioxane solutions the solid phase is $C_6Cl_4(OH)_2 \cdot C_4H_8O_2$. From the observed differences of potential the free energies of solvation

(1) Conant, Small and Taylor, *THIS JOURNAL*, **47**, 1959 (1925); Hall and Conant, *ibid.*, **49**, 3047 (1927); Conant and Chow, *ibid.*, **55**, 3745 (1933).

(2) Hall, *ibid.*, **52**, 5115 (1930).

(3) Conant and Chow, *loc. cit.*, p. 3748.

(4) See, e. g., König, *J. prakt. Chem.*, [2] **70**, 33 (1904).

may be readily calculated and are found to agree well with the physical properties of the solvates.

It is clear that the potential of the chloranil electrode may be assumed independent of the solvent only if the electrode materials remain unsolvated under the conditions of the experiment.

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THE VISCOSITY OF H²H²O

Sir:

The great difference between the conductivity of potassium chloride in H²H²O and in H¹H¹O which was found by Lewis and Doody [THIS JOURNAL, **55**, 3504 (1933)], made it desirable to ascertain the viscosity of heavy water. The time required to fill a pipet through a fine capillary, with a known head of pressure, was measured with a stop watch, the apparatus being enclosed in a constant temperature bath. At each temperature the heavy water was compared directly with ordinary pure water. The very close approximation to linearity between viscosity and isotopic composition is shown by the results obtained with water containing 70 and 90% of H². If η_1 and η_2 represent the viscosities of H¹H¹O and H²H²O, η_2/η_1 at 20° was found to be 1.249 by extrapolation from 90% and 1.244 by extrapolation from 70%.

The 90% sample was next compared with ordinary water between 5 and 35°. The results extrapolated to pure H²H²O show η_2/η_1 to be nearly linear with the temperature. The values interpolated at even temperatures are given in Table I, in which the first row gives the values of η_2/η_1 the second reproduces the values of η_1 given in "International Critical Tables," and the third the viscosity (in millipoises) of pure H²H²O obtained by multiplying the numbers in the first row by those in the second. We believe the results to be accurate within 0.5%.

VISCOSITY OF PURE H²H²O

<i>t</i> , °C.	5	10	15	20	25	30	35
η_2/η_1	1.309	1.286	1.267	1.249	1.232	1.215	1.198
η_1	15.19	13.10	11.45	10.09	8.95	8.00	7.21
η_2	19.88	16.85	14.51	12.60	11.03	9.72	8.64

These measurements of the viscosity, together with the measurement of the dielectric constant of H²H²O (accompanying communication), will permit the application of the Onsager equation to the conductivity measurements of Lewis and Doody. Since our experimental measurements of the viscosity were made, values of the viscosity of heavy water, at 20°,

have been given by Selwood and Frost [THIS JOURNAL, 55, 4335 (1933)], but for some reason that we cannot understand, their results do not agree at all with our own.

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GILBERT N. LEWIS
RONALD T. MACDONALD

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THE DIELECTRIC CONSTANT OF H²H²O

Sir:

By balancing capacities in an oscillating radio circuit, we have made a preliminary study of the dielectric constant of water in which the isotope H² constituted over 99% of the total hydrogen. A small cell (0.4 cc.) with parallel platinum plates was tested with various liquids and the capacity was found to be very nearly linear with the dielectric constant. The heavy water was then compared with ordinary conductivity water, at frequencies corresponding to 25, 34 and 40 meters. In the first experiments, the heavy water which had been distilled from sodium hydroxide in a vacuum was found to have a high conductivity ($\kappa = 3 \times 10^{-4}$) which certainly invalidated the results at the longer wave lengths. A somewhat improved cell was then made and the water was again distilled to obtain a conductivity of $\kappa = 1 \times 10^{-5}$ at the beginning and $\kappa = 3 \times 10^{-5}$ after several manipulations, including the filling of the cell. With such small samples it is difficult to obtain a higher purity than this. The conductivity still proved to be too high to give satisfactory results at 40 meters, but at 25° we found D_2/D_1 , the ratio of the dielectric constant of H²H²O to that of H¹H¹O, to be 0.987 at 25 meters and 0.991 at 34 meters, while the value obtained with the more impure water at 25 meters was 0.993. The average of these three values, $D_2/D_1 = 0.990$ at 25°, may also be taken as the ratio at infinite wave length. The only attempt to obtain the temperature coefficient was made with the more impure water. At 10° (25 meters) we found $D_2/D_1 = 0.982$. Here as in all other cases we find the divergence between the two kinds of water increasing with diminishing temperature.

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