

the earth are too great by a factor of two, unless some plausible explanation of the clash of data can be found.

Since writing the above, H. E. Suess<sup>6</sup> has published a letter in which he arrives at a similar result. He concludes that the proposed half-life of  $2 \times 10^8$  yr. for potassium-40 must be incorrect.

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<sup>1</sup> Bleuler, E., and Gabriel, M., *Helv. Phys. Acta*, **20**, 67 (1947).

<sup>2</sup> Gleditsch, E., and Graf, T., *Phys. Rev.*, **72**, 641 (1947).

<sup>3</sup> Clarke, F. W., "Data of Geochemistry", 22 and 36 (5th ed., 1922).

<sup>4</sup> Nier, *Phys. Rev.*, **50**, 1041 (1936).

<sup>5</sup> Clarke, F. W., "Data of Geochemistry", 31.

<sup>6</sup> Suess, H. E., *Phys. Rev.*, **73**, 1029 (1948).

### Structure of the Pigment of *Chromobacterium iodinum*

THE dihydroxyphenazine obtained by catalytic reduction of the pigment of *Chromobacterium iodinum*<sup>1</sup> has been methylated. The resulting dimethoxyphenazine crystallized in yellow needles, m.p. 245–246° (found: C, 69.9; H, 4.4; C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires C, 70.0; H, 5.0 per cent). This compound differs from 1:4-dimethoxyphenazine<sup>2</sup>, m.p. 185°. It has been shown already that synthetic 1:2- and 1:3-dihydroxyphenazines<sup>3,4</sup> differ from the natural product. The conclusion, therefore, is that the pigment contains the two hydroxyl groups in different benzene nuclei of the phenazine skeleton.

The condensation of 3-methoxy-*o*-quinone with 3-methoxy-*o*-phenylenediamine has yielded a mixture of 1:5- and 1:8-dimethoxyphenazines which was separated by chromatography, yielding:

(a) Yellow needles, m.p. 245–246°, not depressed by admixture with the dimethoxy phenazine described above (found: C, 70.4; H, 4.7; C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires C, 70.0; H, 5.0 per cent). The crystalline forms of the two specimens are identical.

(b) Yellow, hair-like needles, m.p. 253–254° (found: C, 70.2; H, 4.7; C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires C, 70.0; H, 5.0 per cent).

The problem of the orientation of the two methoxyl groups in (a) is now being investigated, and a full account of our work will be published elsewhere.

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<sup>1</sup> Clemo, G. R., and McEwain, H., *J. Chem. Soc.*, 479 (1938).

<sup>2</sup> Slack, P. Z., and Slack, R., *Nature*, **160**, 437 (1947).

<sup>3</sup> Hegedus, B., *Feitschrift für E. C. Barell*, 388 (1946).

<sup>4</sup> Clemo, G. R., and Daglish, A. F., *J. Chem. Soc.* (in the press).

### Preparation of Phthalyl-L-Glutamic Acid

IN a recent paper recording the preparation and properties of phthalyl-amino-acids, Billman and Harting<sup>1</sup> claim that the derivative obtained by heating L-glutamic acid with phthalic anhydride at 180–185° is the optically active phthalyl-L-glutamic acid.

While investigating the use of phthalylated intermediates as a means of synthesizing simple peptides containing glutamic acid, we have prepared both phthalyl-L-glutamic acid, m.p. 158–159°,  $[\alpha]_D^{25} = 0.33$  N sodium carbonate =  $-27.4^\circ$  (found: C, 56.5;

H, 4.0; N, 4.9; C<sub>13</sub>H<sub>11</sub>O<sub>6</sub>N requires C, 56.3; H, 4.0; N, 5.1 per cent), and the corresponding racemic acid, m.p. 189–190° (found: C, 56.5; H, 4.0; N, 5.0 per cent). The American authors have not quoted the rotation of their phthalylglutamic acid; but it is evident from its melting point of 188–189° that the derivative described by them is the DL-compound. However, we have repeated their preparation, and although the crude product has measurable optical activity, we have confirmed our earlier observation that the only compound which can be isolated on recrystallization is the racemic acid of melting point 189–190°. Phthalyl-DL-glutamic acid is more satisfactorily prepared by heating phthalic anhydride and a suspension of L-glutamic acid in boiling pyridine. The crude phthalamic acid obtained on evaporating the solvent is then heated with acetic anhydride to close the phthalimide ring, dehydration of the glutamic acid residue occurring simultaneously with the formation of phthalyl-DL-glutamic anhydride. From this the DL-acid is obtained simply by dissolving in warm water.

In order to avoid racemization, which may be due to oxazolone formation under the influence of the acetic anhydride, it is necessary to use a glutamic ester, for example, diethyl L-glutamate, which reacts with phthalic anhydride in cold ether. From the precipitated product, diethyl phthalyl-L-glutamate is readily obtained by the action of thionyl chloride, and hydrolysis with boiling 2N acid gives the phthalyl-L-glutamic acid, m.p. 158–159°.

Both phthalyl-DL-glutamic anhydride and the corresponding L-compound have been condensed with various amino-compounds, including amino-acids, and from the products the phthalyl group has been removed, under conditions which leave the peptide linkages intact, by an adaptation—already considerably exploited<sup>2</sup>—of the well-known hydrazine method.

A full account of these experiments will be published in due course.

Note added on October 22.—Phthalylglutamic anhydride differs from other acylglutamic anhydrides, for example, carbobenzoxy-L-glutamic anhydride, in reacting with ammonia to form the  $\gamma$ -amide, thus affording a direct synthesis of glutamine. Evidence for this important difference is found in the degradation of the phthalyl derivative with sodium hypobromite, eventually to 1:3-diaminobutyric acid, and in the evolution in the van Slyke estimation of 98 per cent of the nitrogen content of the product obtained after removing the phthalyl group.

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<sup>1</sup> *J. Amer. Chem. Soc.*, **70**, 1473 (1948).

<sup>2</sup> King, F. E., and Robinson, Sir Robert (unpublished work).

### Paper Chromatography of the Noble Metals

THE separation of amino-acids by partition chromatography on paper was first described by Consden, Gordon and Martin<sup>1</sup>. A large number of separations of organic compounds has been described since then. I have recently discovered that cations can be separated successfully if the solvent is adjusted suitably to prevent hydrolysis. The solvent selected for study was butanol saturated with N aqueous hydrochloric acid.