

different from adipic acid. Further work is being continued.

P. C. GUHA.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore, India,
April 25, 1936.

¹ Baeyer, *Ber.*, 1892, 25, 2123.

² Meerwein, *J. Pr. Chem.*, 1922, (ii), 104, 180.

A Synthesis of *Cis*- and *Trans*-*dl*-1-*iso*-Propyl Cyclopropane-1:2-Dicarboxylic Acids and a Resolution of the *Cis* Acid. Synthesis of Umbellularic Acid.

In his experiments on the constitution of umbellulone, Tutin¹ obtained as the ultimate product of its oxidation, an optically active dibasic acid, umbellularic acid, $C_8H_{12}O_4$, m.p. 120–121° (α_D) – 89.7° (in $CHCl_3$). Although Tutin believed the acid to be a derivative of methyl *cyclo*-pentane, the experiments of Semmler² definitely fixed its constitution as 1-*isopropyl cyclopropane*-1:2-dicarboxylic acid. The *cis*- and *trans*-*dl*-forms of this acid have now been synthesised.* Also the *cis* acid has been resolved into its optical antipodes and the properties of the latter are identical with those of umbellularic acid.¹

Ethyl α -*isopropyl acrylate*³ adds on ethyl diazoacetate to give ethyl 5-*isopropyl*- Δ pyrazoline-3:5-dicarboxylate, b.p. 158° at 1 mm. and the latter splits off nitrogen at 200°⁴ giving rise to the mixed ester, b.p. 144–48°/28 mm. On hydrolysis this furnishes *trans*-*dl*-1-*isopropyl cyclopropane*-1:2-dicarboxylic acid (m.p. 195°·0 C.)[†] in about 35% yield, the rest being a liquid mixture of unsaturated acids. The *cis* anhydride prepared from *trans* acid by heating with acetylchloride at 180°, boils at about 140°/20 mm. The *cis*-*dl*-acid crystallises from water with one molecule of the solvent (m.p. 95°, sintering 86°). The anhydrous acid melts at 124–125° and passes over to the anhydride at 150°. The chemical properties of these two acids are identical with those of umbellularic acid.¹

On combining *cis*-*dl*-acid with brucine in aqueous solution the salt of the *d*-form separated first, and had the composition $C_{54}H_{64}O_{12}N_4 \cdot 9H_2O$ (α_D^{30}) – 25.63 (in alcohol). The active acid liberated from the salt had (α_D^{31}) + 87.7 (in $CHCl_3$), m.p. 118° with $1H_2O$ about 83°. For obtaining the *l*-acid cinchonidine was employed, when the salt of the *l* form $C_{27}H_{34}N_2O_5$, separated first. The acid liberated had (α_D^{31}) – 81°·13.

The crystalline forms of both the antipodes were in agreement with those cited by Tutin for umbellularic acid.

Full details of the work have been sent for publication elsewhere.

S. K. RANGANATHAN.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore,
June 11, 1936.

¹ Tutin, *J.C.S.*, 1906, 89, 1104.

² Semmler, *Ber.*, 1907, 40, 5019; *Ibid.*, 1908, 41, 3988.

³ Blaise and Luttringer, *Bull. Soc. Chim.*, 1905, (3), 33, 648, 776.

⁴ Buchner and Papendieck, *Annalen*, 1893, 273, 232. von Auwers and König, *Ibid.*, 1932, 496, 252.

* The Synthesis of the *dl*-acids was complete and the resolution of the *cis* acid was in hand when an abstract on the synthesis of umbellularic acid appeared (Rydon, *Chem. and Ind.*, 1936, 55, 294). The method adopted by Rydon, however, is different and we thought it fit to continue our work and place the results for publication.

† The figures for melting point given in this note are all uncorrected.

Apparatus for the Measurement of Respiratory Exchange in Plants.

FOR the measurement of respiratory gaseous exchange in plants Haldane's gas-analysis apparatus is commonly employed. Although highly accurate, the apparatus in its original form¹ is inconvenient and rather cumbersome for respiration studies in plants. Carpenter² has replaced the long, cylindrical levelling tube which is rather difficult to manipulate, by a small mercury bulb which is easily handled. The original Haldane apparatus contains a combustion pipette for the oxidation of carbon monoxide or methane. This pipette was utilised to advantage by Carpenter² for the absorption of oxygen by means of moist phosphorus. It has the advantage over potassium pyrogallate that it does not have to be renewed so frequently and that the absorption can be carried out without the continuous raising and lowering of the mercury levelling bulb. In this Laboratory, however, during the course of investigations on the gas-storage of tropical fruits the apparatus has been further simplified and the technique for the measurement of respiratory exchange in plants considerably improved. The gas sampler employed by Haldane has been dispensed with, the measuring pipette serving as a sampling appliance as well. The potassium pyrogallate bulb (together with its accessory bulbs) has been replaced by a phosphorus bulb of the type employed by Carpenter,²

thus minimising the breakages which frequently occur in this apparatus. For the simultaneous determination of the CO_2 evolved and the oxygen absorbed, the plant organs are enclosed in air-tight chambers which provide for the removal of test portions for analysis. The use of respiration chambers with rubber stoppers is open to criticism, as rubber has a tendency to absorb CO_2 and also to let it diffuse through it. To circumvent this difficulty, two new types of respiration chambers have been constructed into which the various gas mixtures are easily introduced and which are trustworthy in regard to their air-tightness. A method, similar in principle to the Münzer-Neumann method³ for the calibration of Warburg and Barcroft manometers, is suggested for the calibration of the respiration chambers after the introduction of the plant material.

The measuring pipette P of the apparatus (Fig. 1) can be put in communication either with the KOH bulb C or the phosphorus bulb D by means of the Friedrich-Greiner tap F. The phosphorus bulb is similar in construction to the combustion pipette employed by Haldane except that the ignition tubes inside it have been removed and a water levelling bulb added. The bulb is filled with stick yellow phosphorus of suitable length so that 21. c.c. of gas can be introduced into it. The measuring pipette P and the compensation pipette P' are enclosed within a glass jacket, the water in which is kept stirred by means of an air-blower B. The manipulation, in brief, is as follows. The air in the apparatus is first freed from CO_2 and oxygen in order that all of the capillaries may be filled with nitrogen. Subsequent to this, the 3-way stopcocks G and H and the tap F are turned

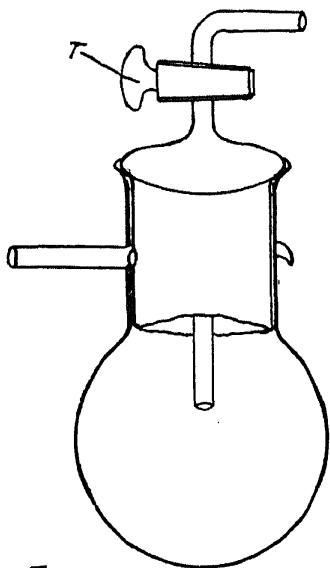


FIG. 3.

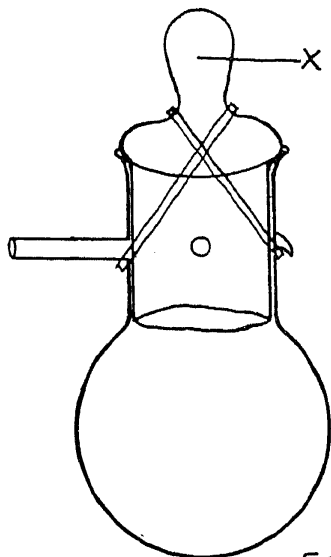


FIG. 2.

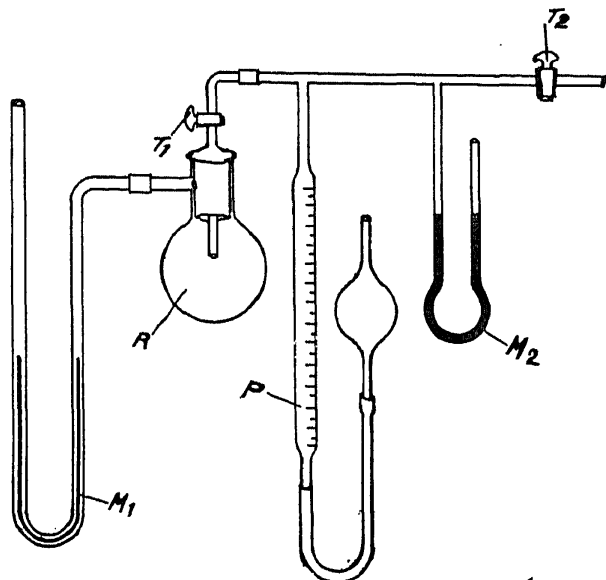


FIG. 4.

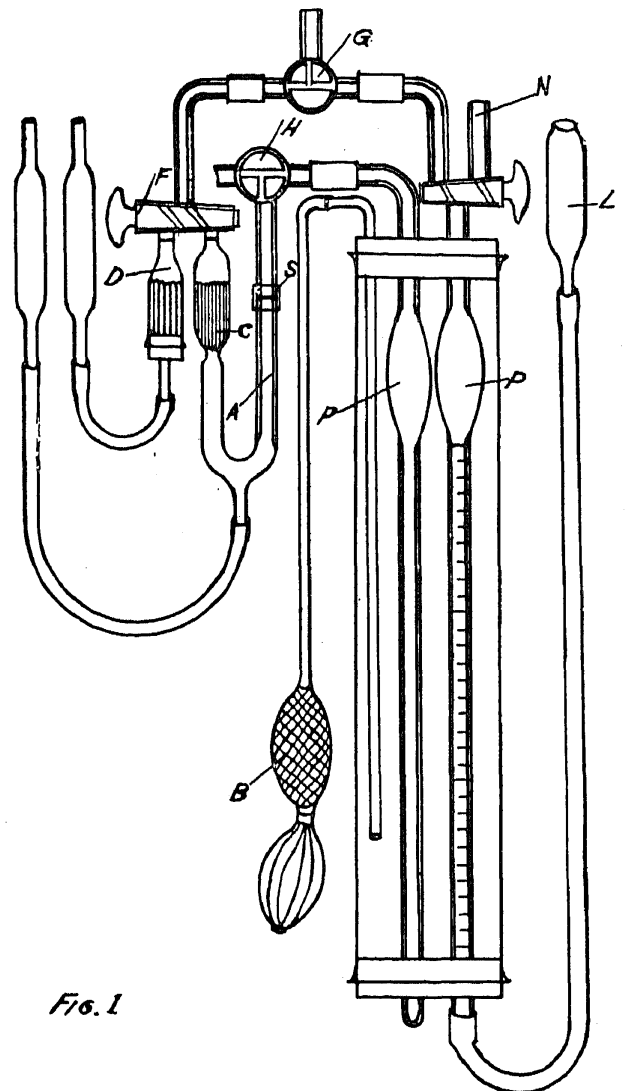


FIG. 1

An Adaptation of Haldane's Apparatus for the Measurement of Plant Respiration.

