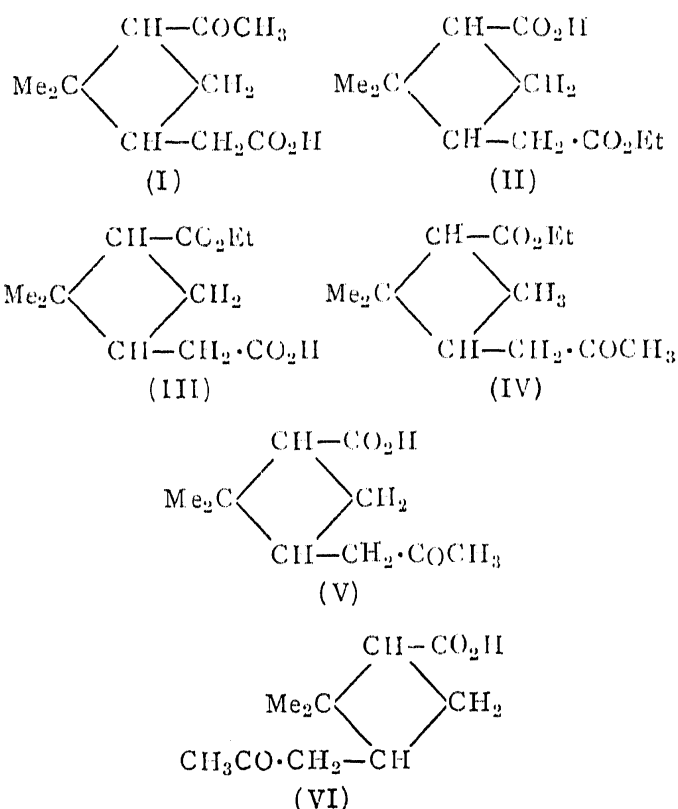


**Trans-1-acetyl-2:2-dimethylcyclo-
butane-3-carboxylic Acid: An Isomer of
Pinonic Acid.**

In an attempt to synthesise pinic acid mono-ester (II) by (i) partial esterification of pinic acid, and (ii) partial hydrolysis of diethyl pinate, with an object to convert the acid-chloride of (II) by Blaise reaction into pinonic acid (I), the isomeric acid ester (III) has been obtained in very good yield by the latter method. The mono-acid ester (III, b.p. 158–60°/5 mm.; d_{30}^{20} , 1.0693; n_D^{30} , 1.4532) readily gives the acid-chloride (b.p., 118°/4.5 mm.) with thionyl chloride, which in its turn with zinc methyl iodide yields the ketonic ester (IV, b.p. 118–119°/5 mm.; semicarbazone, m.p. 134°). The ketonic ester on hydrolysis, furnishes the corresponding acid (V, semicarbazone, m.p. 186°). The difference of this acid from both the *trans* and *cis* varieties of pinonic acid (I) obtained from pinene, has been established by comparing the melting points of the semicarbazones and the acid (III) should, therefore, have the constitution assigned to it. Hence, it was expected that the structure of the ketonic acid should be identical with that of orthodonic acid (V) obtained by Fujita¹ by the oxidation of orthodene from orthodon lanceolatum. In view of the difference between the melting points of the semicarbazone of our acid (m.p. 186°) and that of orthodonic



acid (m.p. 116–18°), it seems that orthodonic acid may have the *cis*-configuration while our acid (VI) being derived from *trans*-pinic acid² represents the *trans* variety.

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¹ *J. Chem. Soc., Japan*, 1933, **54**, 1811.

² *Ber.*, 1937, **70**, 1505.

**Redox Systems in the Latex of *Carica
papaya*.**

THE latex obtained from *Carica papaya* contains a remarkably large amount of sulfhydryl compounds, in fact, about ten to twenty times the concentration in any plant or animal source till now known.¹ A fraction of these -SH compounds occurs as glutathione which serves as a natural activator of papain. The search for an enzymic system specific for the reduction of glutathione and SS-compounds to the -SH form, has been actively pursued and a definite lead in this direction has already been given by the work of Hopkins and co-workers. In view of the circumstance that SH-compounds occur in very high concentrations in the latex of *Carica papaya*, it is of interest to enquire whether similar reducing systems are present in it.

Hopkins and Elliot² have established the presence of heat labile SS reducing systems in animal tissues. They showed that molecular oxygen oxidises the -SH compounds present in liver to the SS form and the enzymic systems in this tissue reduce the SS-form back to the SH. In the latex of *Carica papaya* freshly obtained, there are similar SH \rightleftharpoons SS redox systems. Here again the SH is readily oxidised to the SS by molecular oxygen. The presence of reducing systems is shown by the circumstance, that when the latex, dispersed in phosphate buffer (pH 7.4) is aerated, the concentration of SH does not fall during the earlier part of the process, but remains constant (or sometimes even slightly increases). The curves shown in Fig. 1 are typical of several experiments. It will be seen that in the earlier part of aeration the reduction processes equalise (and sometimes even out-

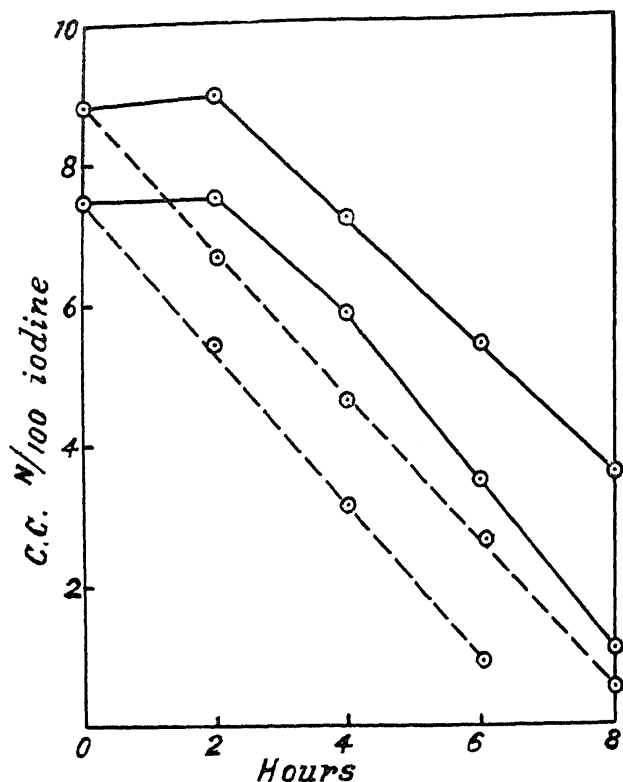


Fig. 1.

Changes in the Concentration of -SH during continuous aeration of the latex (1 gm. in 20 c.c. Buffer Hn 7.4) from *Carica papaya* at 25° 0 C.

Continuous lines .. Normal curves

Broken lines .. Latex previously heated.

(The two sets of curves represent two different specimens of the latex.)

balance) oxidation. When the latex is heated, however, the latent period during which the SH concentration remains constant, is not found and the SH constant, as determined by the method of Kunhau,³ falls even from the commencement of the aeration, thus indicating the enzymic nature of the systems involved.

When SS-compounds prepared from the latex by oxidising the SH with iodine or hydrogen peroxide, are added to the latex and incubated, there is a distinct increase in the titrable SH content. This reduction is more prominent when the pulp of *Carica papaya* is employed. But in either case, this reducing property is very much reduced when heated prior to incubation.

The presence of such redox system in the latex of *Carica papaya* is very significant. It is believed that papain activity is due to the -SH form of the protein, the enzyme losing its activity when the SH is oxidised to the SS-compound. The reducing systems present in the latex afford a fine mechanism

for regulating the proteolytic activity of natural papain, the active form being obtained either directly by the reducing systems or indirectly, through the sulfhydryls which are first formed. Further, the presence of glutathione in the latex calls for a closer study of the reducing systems so as to give a deeper insight into the mechanism of respiration of the living cell which is controlled by the glutathione present in it. The results obtained with plant materials on the one hand and animal tissues on the other,⁴ indicate a close parallelism in the enzymic processes involved.

In the light of the recent researches of Hopkins and Morgan⁵ on the relation between ascorbic acid and glutathione, experiments involving the estimation of the SH content as well as the vitamin simultaneously in the latex during aeration have been carried out. The presence of ascorbic acid does not in any way affect the course of the oxidation of SH-compounds. The results confirm the main conclusion of Hopkins and Morgan, *viz.*, that the ascorbic acid is protected from oxidation by the sulfhydryl compounds which coexist with the vitamin.

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¹ Ganapathy and Sastri, *Curr. Sci.*, 1938, **6**, 330.

² Hopkins and Elliot, *Proc. Roy. Soc.*, 1931, **119**, 58.

³ Kunhau, *Biochem. Z.*, 1931, **230**, 360.

⁴ Hopkins and Elliot, *Loc. cit.*

⁵ — and Morgan, *Biochem. J.*, 1936, **30**, 1446.

The Exchange of Moisture between Air Layers near the Ground and Substances like Soils, Plant Leaves, Seeds, etc., Exposed to the Atmosphere.

IN a recent series of papers Ramdas and Katti^{1, 2, 3, 4, 5, 6} have discussed the phenomenon of the diurnal exchange of moisture between a dry soil surface when it contains only hygroscopic water and the air layers near the ground. It was shown that the soil has its *maximum* moisture content at the minimum temperature epoch and its *minimum* moisture content at the maximum temperature epoch. From the morning after sunrise up to the afternoon, the soil surface gives up moisture by evaporation