of the Technological Irradiation Group for their kind co-operation.

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Structure of β-Acylacrylic Acids

In previous publications[1-5] the β-formyl-, β-acetyl- and β-pivaloyl-acrylic acids were investigated by means of their spectra in the ultra-violet and infra-red. This work has been extended to comprise the α-methyl-β-acrylic acid[6,7]. In regard to *cis–trans* isomerism and open or cyclic structure for the preparations used, the infra-red spectra (in the case of acid (5) also by means of the nuclear magnetic resonance) have confirmed the following structures :

(1) β-Formylacrylic acid, m.p. 53–56° C. : cyclic, *cis*
(2) β-Acetylacrylic acid, m.p. 122–125° C. : *trans* (probably with a smaller amount *cis*-open acid)
(3) β-Pivaloylacrylic acid, m.p. 84–85° C. : cyclic, *cis*
(4) β-Pivaloylacrylic acid, m.p. 94–95° C. : *trans*
(5) α-Methyl-β-acetylacrylic acid, m.p. 98–101° C. : cyclic, *cis*

The ultra-violet spectra of compounds (1) and (3) had end-absorption, but (2) and (4) had a maximum at about 220 mμ (in water). The former had, however, more or less a shoulder at 240 mμ, which with increasing *p*H developed to a maximum at 245 mμ, which upon acidification disappeared. With development of the maximum at 245 mμ a maximum or a shoulder appeared at about 320 mμ, indicating a ketonic group. Thus, the ring in these cases should be opened by neutralization. Now, the compound (5) has shown the same behaviour.

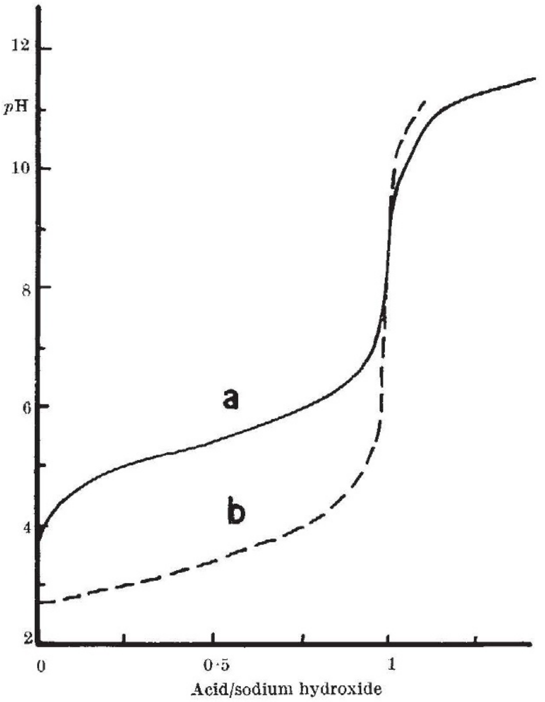

Fig. 1. Titration curves for the compounds given in text, (*a*) cyclic *cis* acids, (*b*) (open) *trans* acids dissolved in water with 0·1 *N* sodium hydroxide, volume about 20 ml.

Regarding the cyclic formula one could expect compounds with this structure to have acidic properties, and therefore it seemed worth while to compare these two categories by means of titrations and *p*H determinations. Fig. 1 gives in short the results ; curve (*a*) refers to the cases (1), (3) and (5), that is, the cyclic *cis* structure, and curve (*b*) to the cases (2) and (4), that is, the (open) *trans* structure. Evidently, this seems to be a complementary method for determining the structure, and it follows that the pK_a values about 5·5 and 3·5 respectively characterize the curves. Back-titration gives the same curves. As from the ultra-violet spectra it must be concluded that the ring opens upon neutralization, it evidently is—if not instantaneously but very rapidly —closed upon acidification. Thus, it seems evident that the maximum at 245 mμ refers to the open *cis* form, which has been proposed previously.

A further report, also including nuclear magnetic spectra for these compounds, will be given elsewhere with a more detailed discussion.

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BIOCHEMISTRY

Occurrence of Keto-Acids in Blood Serum and Urine of Cattle in Comparison with Man, Horse, Sheep and Dog

In connexion with metabolic disorders occurring in cows, such as parturient paresis and acetonæmia, an investigation concerning the keto-acids occurring in blood serum and urine was started. Several authors have carried out work in this field concerning man. Keto-acids are converted into 2,4-dinitrophenylhydrazones, after which they are separated by means of paper chromatography. The 2,4-dinitrophenyl hydrazones are reduced by hydrogen to amino-acids and identified as such. In this way Cavallini *et al.*[1], El Hawary and Thompson[2], Markees[3], Biserte and Dassonville[4] and De Schepper *et al.*[5] showed that the following α-keto-acids occur in human blood : α-ketoglutaric acid, pyruvic acid, α-keto*iso*caproic acid, α-keto*iso*valeric acid and α-keto-β-methylvaleric acid. Moreover, it was shown that pyruvic acid predominates in human blood and α-ketoglutaric acid in human urine[4].

Applying De Schepper's method[5] the keto-acids of bovine serum were converted into 2,4-dinitrophenyl hydrazones and separated by means of chromatography, as well as by electrophoresis combined with evaporation at 6 V./cm. at *p*H 11·7. After reduction with hydrogen and platinum oxide as a catalyst, the amino-acids obtained were examined both by electro-