on log/log paper the curves were straight lines up to at least 100 mg K/l (770 mμ) or 1 000 mg K/l (405 mμ).

When only potassium determinations are concerned, it may be advantageous to use a cooler flame than the air-acetylene one, *e. g.* air-butane. The sensitivity for potassium is about the same, or even higher, and the presence of sodium effects the potassium reading much less *Cf.*[4]. The potassium calibration curves appear to be more linear in this case. However, such an instrument is not sensitive enough for most other elements.

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## α-Thienylsuccinic Acid

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In the course of the present work on optically active thiophene compounds, ethyl thienylcyanoacetate has been prepared[1] and then allowed to react with halogen compounds[2]. A new example of this reaction is the preparation of thienylsuccinic acid from ethyl thienylcyanoacetate and ethyl chloroacetate, yielding ethyl thienylcyanosuccinate, which has then been decarboxylated and hydrolyzed to give thienylsuccinic acid.

Thienylsuccinic acid crystallizes from ethyl acetate as a colourless, microcrystalline powder, melting with decomposition at 156—157° C. From water it is obtained in hemi-spherical crystal aggregates. The difficulty of obtaining well-shaped crystals may indicate that the acid, like the analogous phenylsuccinic acid, is dimorphic[3].

The acid will be resolved in the optical antipodes and the result published later.

*Ethyl thienylcyanosuccinate:* In a round-bottomed, two-necked flask, fitted with a mercury-sealed stirrer and a reflux condenser, were placed 15.0 g (0.077 moles) of ethyl thienylcyanoacetate, 25 g (0.2 moles) of anhydrous potassium carbonate, 30 ml of ethyl chloroacetate and 100 ml of dry acetone. The mixture was refluxed with stirring for 20 hours in an oil bath, the acetone removed by distillation and the residue treated with 50 ml of water to dissolve the inorganic salts. The oily layer was separated, and the water layer extracted three times with ether. The oily and ether layers were then combined, dried with sodium sulphate and distilled *in vacuo.* 13.0 g (0.046 moles) of ethyl thienylcyanosuccinate was obtained. B. p. 200—205° C/12 mm Hg. Yield: 60 %.

*Thienylsuccinic acid:* 13.0 g (0.046 moles) of ethyl thienylcyanosuccinate and 12 g (0.2 moles) of potassium hydroxide, dissolved in alcohol, were warmed on a water bath for five minutes, the potassium carbonate filtered off and washed with alcohol. The filtrate was treated with 20 ml of water and refluxed in an oil bath, until no more ammonia escaped (24 hours). The alcohol was removed by distillation and the residue acidified with dilute hydrochloric acid. The thienylsuccinic acid was obtained as a yellow oil, which dissolved in warm water. The water solution was boiled with charcoal and filtered. After cooling, 6.0 g (0.030 moles) of thienylsuccinic acid was obtained as light yellow, hard crystal aggregates. Yield: 65 %. The acid was recrystallized from a small amount of ethyl acetate. M. p. 156–157° C with decomposition.

$C_8H_8O_4S$

| | Equiv. wt. | C | H | S |
|---|---|---|---|---|
| Calc. | 100.1 | 47.99 | 4.03 | 16.01 |
| Found | 100.6 | 48.05 | 4.08 | 16.08 |

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# A Spraying Reagent for Paper Chromatograms Which is Apparently Specific for Ketoheptoses

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Pentoses, glucuronic acid and certain heptoses are known to give a bluish green colour with Bial's reagent (orcinol dissolved in hydrochloric acid, to which $FeCl_3$ is added as catalyst [1]). Attempts to use this reagent for the detection of ketoheptoses (sedoheptulose and D-mannoheptulose) on paper chromatograms were unsuccessful, as the mineral acid attacked the paper. By using trichloroacetic acid instead of hydrochloric acid, however, we obtained serviceable results. When an aqueous solution of orcinol and trichloroacetic acid was used the resulting spots were diffuse as the sugars migrate from wet to dry regions on the filter paper [2]. If on the other hand, the reagents are dissolved in water-saturated *n*-butanol [2], well-defined spots are obtained. After a number of experiments we have arrived at the following reagent:

| | |
|---|---|
| Orcinol | 0.5 g |
| Trichloroacetic acid | 15 » |
| *n*-Butanol (water-saturated) | 100 ml |

Owing to rapid esterification the reagent it rather instable. It ougth to be kept in a cold place and not to be used for more than 6–8 days after preparation.

After the paper has been dried, it is sprayed with the reagent and heated at 105° C for 15–20 minutes.

Table 1 shows how the various sugars behave under this treatment. For carrying out the reaction we used about 0.1 mg of each sugar.

As we have not had any aldoheptoses at our disposal, we have not yet tested whether the reagent gives any colour with these. Of the sugars we have tested it is, however, only the ketoses which react. The two heptoses which have hitherto been found in Nature are both ketoheptoses.

*Table 1.*

| Sugar | Colour produced in the reaction |
|---|---|
| Sedoheptulose | Bluish green |
| Mannoheptulose | » » |
| Fructose | Yellow |
| Sucrose | » |
| Glucose | No colour |
| Galactose | » » |
| Arabinose | » » |
| Xylose | » » |
| Ribose | » » |
| Rhamnose | » » |
| Glucuronic acid | » » |

The reagent is useful for, *inter alia*, paper chromatographic studies of the distribution of ketoheptoses in the vegetable kingdom, a research in which we ourselves are at present engaged.

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