removed by distillation, the residue acidified with dilute hydrochloric acid, and the precipitated acid dissolved in ether. After removing the ether 11.2 g (0.047 moles) of thenylthienylacetic acid were obtained. Yield 98 %. The crude acid was recrystallized from dilute formic acid and finally from petrol (b. p. 60—70° C). M. p. 90.5—92.5° C.

	Equiv. wt.	C	H	S
$C_{11}H_{10}O_2S_2$ Calc.	238.3	55.44	4.23	26.91
Found	238.8	55.19	4.12	26.78

Ethyl thenylphenylmalonate: In a round-bottomed, two-necked flask, one neck being fitted with a reflux condenser, 50 ml of absolute alcohol were placed, and then, through the other neck, 4.6 g (0.20 moles) of sodium, cut in pieces. When the sodium had reacted (at the end of the reaction, the flask had to be warmed in an oil bath), 47.0 g (0.20 moles) of ethyl phenylmalonate was added through a dropping funnel. Then 26.5 g (0.20 moles) of thenyl chloride were added, and the mixture heated in an oil bath, until the reaction had ceased. The alcohol was removed by distillation, and water was added to dissolve the sodium chloride, the oily layer separated and the water layer extracted three times with ether. The ether and oily layers were combined, dried with anhydrous calcium chloride and distilled. 36.0 g (0.11 moles) of thenylphenylmalonate were obtained as a light yellow oil, boiling at 185—195° C/9 mm Hg. Yield 55 %.

Thenylphenylacetic acid: In a round-bottomed flask, fitted with a reflux condenser, were placed 36.0 g (0.11 moles) of ethyl thenylphenylmalonate and 10.0 g (0.44 moles) of sodium hydroxide, dissolved in dilute alcohol. The mixture was boiled for one hour in an oil bath. The alcohol was removed by distillation, the residue acidified with dilute hydrochloric acid, the precipitated oily acid dissolved in ether and the ether removed. 22 g (0.095 moles) of thenylphenylacetic acid were obtained. Yield 86 %. The crude acid was recrystallized from petrol (b. p. 60—70° C). M. p. 71.5—72.0° C.

	Equiv. wt.	C	H	S
$C_{13}H_{12}O_2S$ Calc.	232.1	67.21	5.21	13.49
Found	231.5	66.89	5.07	13.58

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The High Rotatory Power of Cystine

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In a recent publication[1] Fieser has drawn attention to the high rotatory power of cystine already pointed out by van't Hoff. While the other acyclic amino acids, including cysteine, are characterized by low specific rotations (about 10°), cystine shows the remarkable value $[\alpha]_D = -214°$ (acid solution). The rotation is greatly dependent on the pH of the medium and in alkaline solution much lower values are reported. According to Fieser, the rotation of cystine appears as extraordinary today as it did to van't Hoff in 1898. As a possible explanation he suggests the formation of hydrogen bonds between the carboxyles and the amino groups, resulting in an endocyclic ring structure.

It is well known that ring formation often exerts a great influence on the rotatory power. In the case of cystine, however, there is another factor to take into consideration, *viz.* the presence of a disulphide group, —S—S—. The specific rotations of some disulphide acids are given in Table 1. In all cases, the activity is greatly influenced by the nature of the solvent. The disulphide-di-*α*-propionic (dithiodilactic) acid (I) has a remarkably high rotation, especially in dilute hydrochloric acid. The rotation of the dithian-dicarboxylic acid (II) and the disulphide-di-*α*-phenylacetic acid (III) are of the same order of magnitude. Thus, in this case neither the ring formation nor the presence of aromatic groups produces any marked increase in the activity. In all these cases, the disulphide group is directly attached to the asymmetric carbon atoms.

In cystine the disulphide group is one carbon atom removed from the centres of asymmetry, and its influence would thus be expected to be less pronounced. In the course of investigations on steric relationships, the author has recently prepared the optically active disulphide-di-*β*-*iso*butyric acid (IV), where the position of the sulphur atoms is the same as in cystine. This compound has a lower activity than acids I—III, but it is quite comparable to that of cystine. In homocystine, described by du Vigneaud and collaborators [2], the disulphide group is two carbon atoms removed from the centres of asymmetry. Here we have $[\alpha]_D = -77°$ (acid solution). The value is lower than for cystine, but obviously higher than for the common acyclic amino acids.

It can thus be said that the high optical activity of cystine is only what could be expected with regard to the presence of a disulphide group and its position in the molecule.

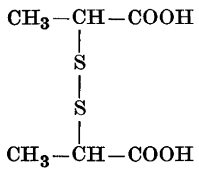
Experimental. The activity values for *disulphide-di-α-propionic acid* (I) are quoted from Bernton [3] and those for *dithian-di-carboxylic acid* from an earlier publication by the author [4].

The (−)-*disulphide-di-α-phenylacetic acid* (III) was prepared from (−)-ethylxanthogene-phenylacetic acid [5]. The particulars will be described in a later publication.

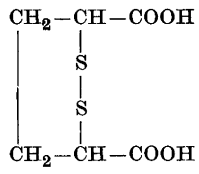
0.2308 g acid: 12.98 ml 0.1065 *N* NaOH: $C_{16}H_{14}O_4S_2$ (334.4)

Equiv. wt. Calc. 167.2 Found 167.0

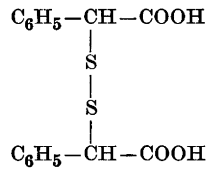
0.1099 g acid dissolved in dilute ammonia to 10.00 ml; $2\alpha = -7.025°$. $[\alpha]_D^{25} = -319.6°$. — 0.1171 g acid dissolved in ethanol to 10.00 ml: $2\alpha = -5.945°$.



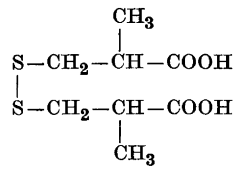
(I)



(II)



(III)



(IV)

Tab. 1. $[\alpha]_D^{25}$ *for the acids I—IV in different media.*

	I	II	III	IV
Dilute hydrochloric acid	+ 430.2°	+ 126°	—	— 151°
Neutr. water solution	+ 152.9°	— 335.8°	— 319.6°	— 219.7°
Ethanol (abs.)	+ 236.6°	— 194.8°	— 253.8°	— 40.2°

$[\alpha]_D^{25} = -253.8°$. The acid is practically insoluble in water and dilute hydrochloric acid.

The preparation of optically active *disulphide-di-β-isobutyric acid* (IV) met with some difficulties. The inactive acid described by Larsson [6] is probably a mixture of racemic and *meso*-acid, and experiments with different alkaloids gave no resolution. The ethylxanthogene-*β-iso*butyric acid is liquid at room temperature and difficult to obtain in a state of purity [7], but the methylxanthogene derivative is crystallised and can be resolved by means of cinchonidine. After ten crystallisations of the cinchonidine salt from dilute (55 %) acetone, the acid showed $[\alpha]_D^{25} = -71.5°$ (acetone solution). The rotation did not change on further recrystallisation of the salt. The xanthogenic acid was decomposed with ammonia, and the resulting mercapto acid oxidised with iodine. The disulphide acid was recrystallised twice from water, in which it is sparingly soluble at room temperature, and obtained as glistening plates. M. p. 124—125°.

0.1227 g acid: 9.68 ml 0.1065 *N* NaOH:
$C_8H_{14}O_4S_2$ (238.3)
Equiv. wt. Calc. 119.2 Found 119.6

0.0220 g acid dissolved in 0.1 N hydrochloric acid to 10.00 ml: $2\alpha = -0.665°$. $[\alpha]_D^{25} = -151°$ — 0.1022 g acid dissolved in dilute ammonia to 10.00 ml: $2\alpha = -4.49°$. $[\alpha]_D^{25} = -219.7°$ — 0.1125 g acid dissolved in ethanol to 10.00 ml: $2\alpha = -0.905°$. $[\alpha]_D^{25} = -40.2°$.

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On the Sulphur Metabolism of *Rhodotorula gracilis*. I. The Importance of Sulphur and Iron for the Formation of Protein and Fat

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It is well known that various microorganisms are able to form considerable quantities of fat if cultivated in nutrient solutions whose nitrogen content is low in comparison with their sugar content. In *Rhodotorula gracilis* [1] the fat content may thus vary between 8 % and 65 %, depending on the composition of the nutrient solution in respect of nitrogen. Parallel with the increase in the fat content there occurs a decrease in the protein content. The latter may vary between 50 % for a normal yeast poor in fat and 12 % for a pronouncedly fat yeast. Probably it is the reduction of the protein content caused by the decrease of the nitrogen content of the nutrient solution which induces fat production.

It seemed of interest to investigate whether a reduction of the protein content of the yeast might be brought about in any other way than by cultivating it in a substrate with a low nitrogen content, obtaining an increased production of fat at the same time. For this purpose we have carried out experiments in which the yeast was cultivated in nutrient solutions containing such small quantities of sulphur or iron in relation to the other nutrient substances as to be insufficient for normal metabolism.

For the cultivation of normal, not strongly fat-producing Rhodotorula gracilis yeast we use a nutrient solution of the following composition: 15 g asparagine — 4.7 g KH_2PO_4 — 3 g $MgSO_4$, 7 H_2O — 1.5 g NaCl — 1.5 g $CaCl_2$, 6