Table 1.

Run no.	Haloketone	Amount g	Solution A g	D/H = 1 min	α/α′
1.	CH_3COCH_3	0.120	0.614	3.5	—
2.	CH_3COCH_2Cl	0.290	1.060	10	3.9
3.	CH_3COCH_2Br	0.212	0.903	10	3.3
4.	CH_3COCH_2I	0.225	0.953	8.5	—
5.	$CH_3COCHCl_2$	0.267	1.237	165	2.8
6.	$CH_3COCHBr_2$	0.231	1.170	60	2.8
7.	$CH_3COCHBr_2$	0.217	0.734	60	2.8
8.	$CH_2ClCOCH_2Cl$	0.420	1.764	60	—
9.	$CH_2BrCOCH_2Br$	0.438	1.608	60	—
10.	$CH_2ClCOCHCl_2$	0.354	1.517	900	1.2
11.	$CH_2BrCOCHBr_2$	*	*	*	*
12.	$CH_3CH_2COCH_3$	0.140	0.662	4.5	1.7
13.	$CH_3CHBrCOCH_3$	*	*	*	*
14.	$CH_3CH_2COCH_2Br$	0.293	1.523	7	—
15.	$CH_3CHBrCOCH_2Br$	*	*	*	*

* Two phases

Experimental. NMR-spectra were recorded with a Varian model A—60 spectrometer. The compositions in the different runs are given in Table 1. The reactions were performed in NMR-tubes at 30°C.

Solution A. 25 ml of heavy water was added to 50 ml of acetyl chloride.

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Studies on Alkylsulfinylcarboxylic Acids

IV. The Reduction of *cis*- and *trans*-β-Ethylsulfinylcrotonic Acids by Means of Iodide in Acid Solution

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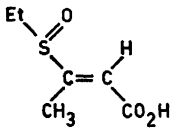
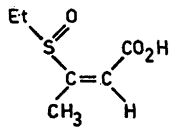
The two isomeric β-ethylthiocrotonic acids (I and II)* have previously been studied by some authors,[1-3] but the corresponding sulfinyl- and one of the sulfonyl-acids have not been reported. In order to obtain further information concerning the mechanism of the reduction of β-alkylsulfinylcarboxylic acids in acidic iodide solution, the two geometric isomers of β-ethylsulfinylcrotonic acid were regarded as suitable compounds for study. As an explanation for the great reactivity of the saturated β-compounds in this reaction, the for-

* The figures refer to the experimental part of this work.

mation of a cyclic intermediate was suggested earlier.[4] Of the two acids (III and IV), however, only one, the *trans*-form,* is capable of forming such a cyclic intermediate. It was therefore of great interest to perform a kinetic study of the reduction of each compound in order to compare the reaction velocities, since the *trans*-form (IV) should react much faster than the *cis*-form (III).



III



IV

The acids III and IV were prepared from the corresponding sulfide-acids through oxidation with hydrogen peroxide in acetone. The sulfones were obtained by oxidation with peracetic acid. It is important to note that the assignment of configurations is the one stated by Jones *et al.*[2] for the sulfide-acids (I and II) which is opposite to that given by Autenrieth.[1]

The sulfinyl-acids were reduced under the same conditions *viz.* in a 0.2 M sodium iodide solution in 2 M perchloric acid at 25°C. The initial concentrations were 5 mM, and the reaction was intended to be followed by titration of the liberated iodine with sodium thiosulfate at various times, *t*, in the same way as described earlier.[5] When such an experiment was carried out with the *cis*-form, it was found that no significant amount of iodine had been liberated after more than three days. With the *trans*-form, however, there was such a rapid formation of iodine that no rate constant could be determined. A very slow consumption of the iodine thus formed, probably due to addition of iodine to the double bond in the unsaturated sulfide-acid formed in the reaction, could also be detected, but is was not followed kinetically.

A test was made to see if any of the two unsaturated sulfide-acids consumed iodine at any considerable rate, and in each case a very slow reaction was observed. The corresponding sulfoxides (III and IV) were totally unaffected by iodine. Consequently, on the basis of these results the authors cannot say that the *cis*-form is not reduced at all, because there is the possibility of a very slow reduction with the liberation of iodine, followed by a more rapid (but still slow) addition to the double bond, so that the net result will be no detection of iodine. Thus it is not easy to say if the *cis*-form is reduced at a slow rate or not, but is is

* Nomenclature according to Ref. 2.

Table 1. Number of equivalents of bromine consumed for the various compounds investigated. (The Roman figures refer to the experimental part of this work).

Compound number	Temperature (°C)	Time (min)	Number of equivalents
I	20	5	7.1
	50	15	7.9
II	20	5	4.2
	50	15	4.8
III	20	15	0.1
	50	15	1.2
IV	20	15	1.9
V	20	15	0.0
VI	20	15	0.1

obvious that this rate is almost negligible in comparison with the rate of reduction of the *trans*-form.

It was also of interest to prepare the two isomers of β-ethylsulfonylcrotonic acid in order to compare the *cis*- and *trans*-forms of β-ethylthio-, β-ethylsulfinyl-, and β-ethylsulfonylcrotonic acid in their behaviour towards bromine. Each compound was titrated with bromide-bromate according to a method described by Larsson [6] and previously used by one of the present authors.[7] Various times and temperatures were used and the results are shown in Table 1. It can be seen that the two sulfones are quite unaffected, *i.e.* there has been no addition of bromine to the double bond, in agreement with what Autenrieth found for the *cis*-compound.[8] The sulfides, however, consume different amounts of bromine; the *cis*-form more than 7 equivalents indicating an oxidative C—S bond scission as the last step, which is similar to the results obtained by Shipley.[9] The *trans*-form, on the other hand, takes up no more than 5 equivalents at 50°C. In both cases the first step is likely to be an addition of bromine to the double bond, followed by oxidation to the sulfoxide. Then the observable difference should be the rate of oxidation to sulfone. The reactions between the sulfoxides and bromine will require further investigation.

Experimental. cis-*β-Ethylthiocrotonic acid (I)* was prepared according to Jones *et al.*[2] It was recrystallized from a water-ethanol mixture. M.p. 90.0—91.0° (Ref. 2: 90.5°). (Found: C 49.5; H 6.92; S 22.0; equiv. wt. 145.9 (NaOH). Calc. for $C_6H_{10}O_2S$: C 49.3; H 6.89; S 21.9; equiv. wt. 146.2).

trans-*β-Ethylthiocrotonic acid (II)* was obtained by the method described by Autenrieth.[1] M.p. 114.0—115.0° (Ref. 2: 114.0—114.2°). (Found: C 49.35; H 7.00; S 21.9. Calc. for $C_6H_{10}O_2S$: C 49.3; H 6.89; S 21.9).

cis-*β-Ethylsulfinylcrotonic acid (III)*. To 7.3 g of I, dissolved in 110 ml of acetone, was added a hydrogen peroxide solution in a 50 % excess of the amount calculated for the oxidation to sulfoxide. The solution was kept at about 0° for 3 days. The acetone was allowed to evaporate, the residue was dried in a vacuum-desiccator over sulfuric acid and finally washed with dry ether. The product was recrystallized from ethyl acetate + carbon tetrachloride yielding large crystals of m.p. 90.5—91.4°. In this way 3.5 g were obtained. (Found: C 44.1; H 6.17; S 19.7; equiv. wt. 163.2 (NaOH). Calc. for $C_6H_{10}O_3S$: C 44.4; H 6.21; S 19.8; equiv. wt. 162.2). ν_{SO}: 1010 cm^{-1} (KBr).

trans-*β-Ethylsulfinylcrotonic acid (IV)*. An attempt to prepare IV in the same way as described for III resulted in a recovery of the starting material (II). Therefore, a longer time and a higher temperature were used, but otherwise the method was the same. To a solution of 0.74 g of II dissolved in 7 ml of acetone a 20 % excess of hydrogen peroxide was added. The solution was kept one day at about 0° and 3 days at room temperature. The yield was 0.39 g of m.p. 97—99°. A small amount of this product was recrystallized from ethyl acetate + carbon tetrachloride giving crystals of m.p. 99.0—100.0°. (Found: C 44.4; H 6.08; S 19.6; equiv. wt. 158.5 (NaOH). Calc. for $C_6H_{10}O_3S$: C 44.4; H 6.21; S 19.8; equiv. wt. 162.2). ν_{SO}: 990 cm^{-1} (KBr).

cis-*β-Ethylsulfonylcrotonic acid (V)*. In order to obtain a complete oxidation to sulfone the use of peracetic acid was found to be most suitable. A solution of 1.0 g of I dissolved in 10 ml of dry ether was cooled to 0°. A peracetic acid solution (containing 13 % peracetic acid in acetic acid and prepared from acetic anhydride and hydrogen peroxide [10]) was added in a 20 % excess of the amount calculated for the oxidation to sulfone. The reaction mixture was allowed to stand one day at 0° and then 5 h at room temperature. After that the treatment was the same as for the synthesis of III. The product was recrystallized from toluene and white needle-shaped crystals were formed. 1.1 g was obtained in this way. M.p. 97.5—98.0° (Ref. 8: 98°). (Found: C 40.5; H 5.65; S 17.9; equiv. wt. 180.0 (NaOH). Calc. for $C_6H_{10}O_4S$: C 40.4; H 5.66; S 18.0; equiv. wt. 178.2).

trans-*β-Ethylsulfonylcrotonic acid (VI)*. The same method as described for the synthesis of V was used and a recrystallization from toluene was undertaken. Starting with 0.24 g of II, the result was 0.16 g of a substance with m.p. 101.5—103.0°. (Found: C 40.4; H 5.65; S 18.0. Calc. for $C_6H_{10}O_4S$: C 40.4; H 5.66; S 18.0).

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Collagen of Lamprey

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The amino acid composition of the collagen varies between the species.[1] Also the distribution of the subunits has been studied in the collagens of various vertebrates both by CM-cellulose column chromatography,[2,3] and by starch gel electrophoresis,[4] but thus far the qualitative pattern[5] of α1, α2, β_{11} (= β2), β_{12} (= β1) and X-units seems to have been similar. The only clear exception is the subject of this note, namely the collagen of lamprey (*Petromyzon fluviatilis*), which yields a different and simple pattern.

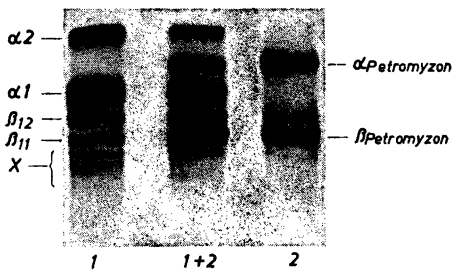

Fig. 1. Starch gel electrophoretic patterns of heat-denatured neutral salt-soluble collagens. *1* control sample from guinea pig skin, *2* sample from lamprey skin, *1+2* mixture.

The neutral salt-soluble collagen was prepared from the skins of adult lampreys according to Gross[6] with slight modifications. The preparations were subjected to starch gel electrophoresis,[5,7] and the pattern is shown in Fig. 1 and compared to a corresponding sample from guinea pig. There are only two main bands and from sedimentation analysis (courtesy by Dr. Tapio Hollmén from our laboratory) we know that the total collagen preparation from lamprey contained two fractions with the same sedimentation velocities as α and β. We believe that the more rapid band represents α and the slower β in the molecular size, but have no suggestion on the intermediate band. The effect of pH on the electrophoretic migration was studied at wide range and then the $\alpha_{Petromyzon}$ resembled the conventional α1 and $\beta_{Petromyzon}$ the β_{11}. The amino acid composition of the collagen of lamprey differs from the collagen of mammals, *e.g.*, by the high content of lysine.

These findings will be reported in full elsewhere, and further experiments are in progress to show whether the collagen of lamprey represents an ancestral form.

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