ACTA CHEMICA SCANDINAVICA 16 (1962) 599–606

Studies on the Chemistry of Lichens

16 *. The Absolute Configuration of Roccellic Acid

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Dedicated to Professor *Holger Erdtman* on his 60th birthday

The configurations at the two asymmetric centres of roccellic acid have been established by degradation of its two isomeric monomethylesters (*8*) and (*16*), to (+)-2L-methylpentadecanoic acid (*11*) and (+)-2L-ethyltetradecanoic acid (*19*), respectively. Roccellic acid must thus be (+)-2L-methyl-3L-dodecylsuccinic acid (*3*a).

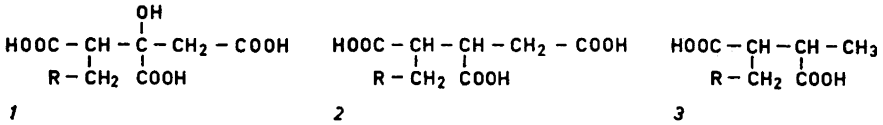
A number of different lichens contain optically active di- and tricarboxylic acids of the types *1*—*6* [1] (Chart I). It is possible that these acids are derived from alkylated citric acids (type *1*, Chart I). Protolichesterinic acid (*4*a), for example, may be formed from *nor*caperatic acid [2] (*1*, R = $C_{13}H_{27}$, Chart I, II). Nephrosterinic acid (*4b*) and roccellic acid (*3*a) could be formed in similar ways. These transformations should not affect the configuration at the asymmetric carbon atom which is shown in Chart II and common to the acids of the types *1*—*5*. The elucidation of the absolute configuration of some of these acids might therefore be of interest in relation to their biosynthesis. With this possibility in mind, the configuration of the simplest member of the group, roccellic acid (*3*a), has been determined.

DEGRADATIVE WORK

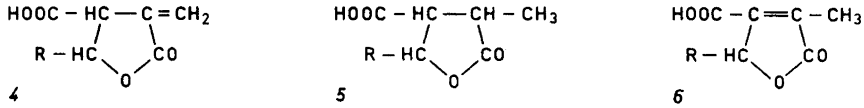
Since a dodecyl group has higher steric requirements than a methyl group, it was possible to prepare the two isomeric monomethyl esters of roccellic acid, (*8*) and (*16*), in a pure state. The monomethylester (*8*), m.p. 45.5—47.5°, was made by treating roccellic acid anhydride (*7*) with dry methanol and the other (*16*), m.p. 56—58°, by hydrolysing dimethyl roccellate (*15*) with an equivalent amount of sodium hydroxide. The monoester (*8*) was decarboxyla-

* Part 15. Lindberg, B. and Meier, H. *Acta Chem. Scand.* 16 (1962) 543.

Chart I

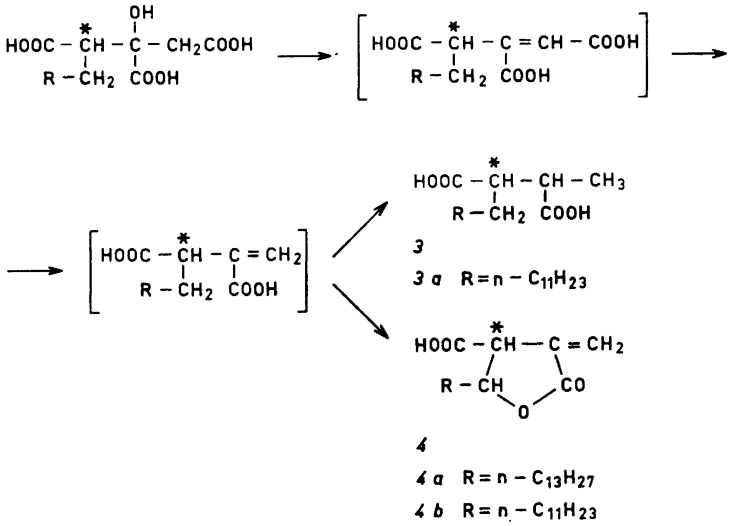


1 *2* *3*



4 *5* *6*

Chart II



ted by the Hunsdiecker reaction to the bromoester (*9*) which was debrominated with zinc-acetic acid to the ester (*10*) and finally hydrolysed to give (+)-2-methylpentadecanoic acid (*11*; Chart III). Similarly, the monoester (*16*) gave (+)-2-ethyltetradecanoic acid (*19;* Chart IV).

The rotatory dispersion curve * of the morpholinethiocarboxamide (*13*) of (+)-2-methylpentadecanoic acid indicated an L-configuration which was also expected from analogy (*cf.* Ref.[4]). The rotatory dispersion curve of the (+)-2-ethyltetradecanoic acid derivative (*21*), however, failed to show the configuration of this compound. Since roccellic acid anhydride (*7*) is almost optically inactive and a *meso*-form might be expected to have a low rotation due to intramolecular compensation, an L-configuration seemed most probable also for (+)-2-ethyltetradecanoic acid. By stereospecific synthesis the L-configuration was confirmed for both (+)-2-methylpentadecanoic acid (*11*) and for (+)-2-ethyltetradecanoic acid (*19*).

* The measurements and the interpretation of the results were done by Miss A. M. Weidler, Dept. of Chemistry, Stanford University, Calif., U.S.A.

Chart III

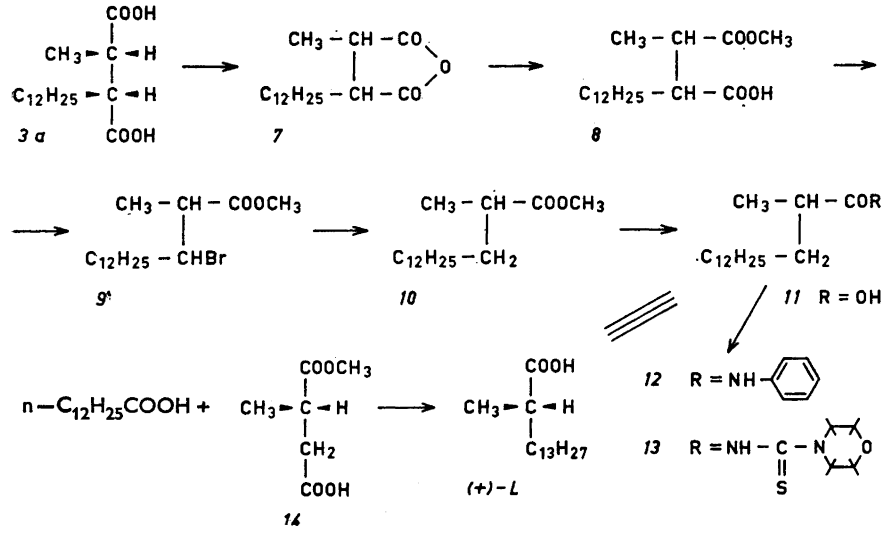
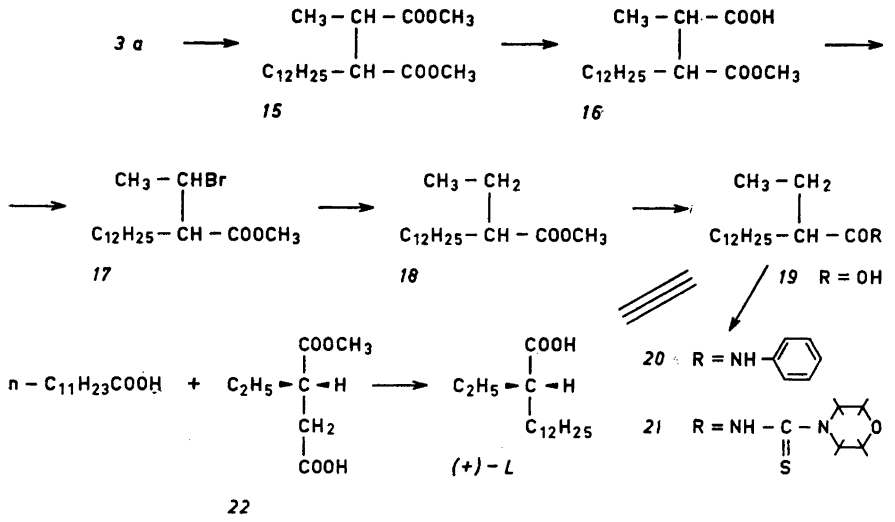


Chart IV



SYNTHETIC WORK

(—)-Methyl 3-carboxy-2L-methylpropanoate (*14*) was made by the procedure described by Ställberg [3]. Mixed electrolysis with tridecanoic acid in methanol containing a small amount of sodium gave (+)-2L-methylpentadecanoic acid (*11*) identical with the degradation product from roccellic acid, although with a slightly higher rotation (*cf.* Ref. [4]).

Similarly, (—)-methyl 3-carboxy-2L-ethylpropanoate (22) was prepared from diethyl allylethylmalonate *via* (—)-2L-ethylpent-4-enoic acid. Since the decarboxylation of allylethylmalonic acid gave a lactone as the main product, the monoethylester of allylethylmalonic acid was decarboxylated and then hydrolysed to 2-ethylpent-4-enoic acid. Several recrystallisations of the quinine salt from acetone gave about 80 % optically pure (—)-2L-ethylpent-4-enoic acid which was methylated and oxidized to (—)-methyl 3-carboxy-2L-ethylpropanoate (*22*) by potassium permanganate in acetone. The configuration and the optical purity of this compound were established by hydrolysis to (—) 2L-ethylsuccinic acid. Mixed electrolysis of (—)-methyl 3-carboxy-2L-ethylpropanoate and lauric acid gave a small amount of (+)-2L,5D-diethyladipic acid and partially racemized (+)-2L-ethyltetradecanoic acid (*19*) having a melting point a few degrees lower than the acid obtained by degradation of roccellic acid. However, the melting point of the synthetic sample was slightly raised on admixture with the degradation product, the infra-red absorption curves of the two acids were identical and the anilides were identical apart from the lower rotation of the synthetic material. A mixture of (—)-2D-ethyltetradecanoic acid (0.010 g) and (+)-2-ethyltetradecanoic acid (0.050 g) from roccellic acid was further identical with the synthetic (+)-2L-tetradecanoic acid in all respects. The acid obtained by degradation of roccellic acid must thus be (+)-2L-tetradecanoic acid (*19*), establishing roccellic acid as (+)-2L-methyl-3L-dodecylsuccinic acid (*3a*; Chart III).

EXPERIMENTAL

Melting points were determined on a Kofler block. Infra-red absorption spectra were taken on a Perkin-Elmer spectrophotometer No. 21, fitted with a sodium chloride prism. The compounds were measured in KBr discs. Microanalysis were carried out by Dr. A. Bernhardt, Mülheim Germany.

Gas chromatography was done on a Pye Argon gas chromatograph, using Apiezon M as the stationary phase and a column temperature of 215°.

Column chromatography was done on silica gel (Gebr. Herrman, Köln, Em 0.15—0.30 mm) using increasing concentrations (0—100 %) of ether in light petroleum (40—60°) as developer.

Roccellic acid (*3a*) was isolated from *Crocynia membranacea* (Dicks.) Zahlbr.[5] M.p. 130.5—132°, $[\alpha]_D^{20}$ + 18.0° (EtOH, *c* 1.94), lit.[6] m.p. 131°, $[\alpha]_D$ + 17.4°.

Roccellic anhydride (*7*). Roccellic acid (12 g) was refluxed with excess of acetyl chloride till the evolution of hydrogen chloride ceased (1.5 h). Distillation of the product at 0.005 mm gave roccellic anhydride (10 g, 89 %) m.p. 26—27.5°, $[\alpha]_D^{20}$ —0.55° ($CHCl_3$, *c* 7.35).

Dimethyl roccellate (*15*) was obtained by methylation of roccellic acid with ethereal diazomethane. Distillation of the product at 0.005 mm gave dimethyl roccellate, m.p. 28.5—30.5°, $[\alpha]_D^{20}$ + 14.5° ($CHCl_3$, *c* 1.67), lit.[6] m.p. 28—29°.

(+)-*Methyl 2-methyl-3-carboxypentadecanoate* (*8*). Roccellic acid anhydride (9.5 g) was refluxed for 0.5 h with dry methanol. The solution was left overnight and excess methanol was then evaporated at room temperature. Chromatography on silica gel (200 g) gave (+)-methyl 2-methyl-3-carboxypentadecanoate (8.0 g, 80 %), m.p. 45.5—47.5°, $[\alpha]_D^{20}$ + 17.6° ($CHCl_3$, *c* 2.96). (Found: C 68.6; H 10.8; equiv. wt. 314. Calc. for $C_{18}H_{34}O_4$: C 68.8; H 10.8; equiv.wt. 314).

(+)-Methyl *3-bromo-2-methylpentadecanoate* (*9*). The monoester (*8*, 9.2 g) was suspended in water (100 ml) and neutralized with sodium hydroxide (1 N). Addition of silver nitrate (6 g in 100 ml water) gave a white silver salt which was washed thoroughly with

water and dried *in vacuo* for 20 h at 100°. The silver salt was then suspended in dry, boiling carbon tetrachloride and bromine was added till presistant colour (4.3 g). The suspension was refluxed for 15 min and then filtered. The precipitate was washed repeatedly with carbon tetrachloride and the combined washings evaporated. Removal of acidic material and distillation gave (+)-methyl 3-bromo-2-methyl-pentadecanoate (7.5 g, 73 %), b.p. 152—154° (1.0 mm), $[\alpha]_D^{20}$ + 10.5° ($CHCl_3$, *c* 4.06), d_4^{20} 1.080. (Found: Br 22.0. Calc. for $C_{17}H_{33}BrO_2$: Br 22.9).

(+)-*Methyl 2-methylpentadecanoate* (10). A mixture of the bromoester (*9*, 7 g), zinc powder (20 g) and potassium iodide (0.1 g) in acetic acid (100 ml) was heated on a water bath for 45 min. After cooling, (+)-methyl 2-methylpentadecanoate (4.8 g, 88 %) was isolated in the usual way. B.p. 141—144° (0.65 mm) $[\alpha]_D^{20}$ + 11.2° (undiluted, *l* 0.5), $[\alpha]_D^{20}$ + 10.9° ($CHCl_3$, *c* 3.31), d_D^{20} 0.868. The purity was proved by gas chromatography. (Found: Saponif. equiv. 265. Calc. for $C_{17}H_{34}O_2$: Saponif. equiv. 270).

(+)-*2-Methylpentadecanoic acid* (*11*). A solution of the ester (*10*, 2.5 g) in dioxan (100 ml) and water (20 ml) containing potassium hydroxide (6 g) was refluxed for 1 h. The crude acid obtained (1.7 g) was chromatographed on silica gel (35 g), giving (+)-2-methylpentadecanoic acid (0.9 g, 40 %). M.p. 39.5—41.5° (from light petroleum at —70° followed by sublimation), identified with a synthetic sample of (+)-2L-methylpentadecanoic acid by means of mixed melting point and infra-red absorption. $[\alpha]_D^{20}$ + 10.5° ($CHCl_3$, *c* 3.06). (Found: C 75.0; H 12.5; equiv. wt. 252. Calc. for $C_{16}H_{32}O_2$: C 75.0; H 12.5; equiv. wt. 256).

The anilide of (+)-*2-methylpentadecanoic acid* (*12*). (+)-2-Methylpentadecanoic acid (*11*; 0.1 g) was treated with thionyl chloride (1 ml) containing a trace of pyridine for 2 h at room temperature. Excess of thionyl chloride was evaporated *in vacuo* and aniline (0.5 g) added. Addition of dilute hydrochloric acid and filtration gave the anilide of (+)-2-methylpentadecanoic acid (0.1 g, 78 %), m.p. 96—97° (from methanol), identified with a synthetic sample by means of mixed melting point determination and infra-red absorption. $[\alpha]_D^{20}$ + 21.0° ($CHCl_3$, *c* 3.21). (Found: C 79.3; H 11.0; N 4.7. Calc. for $C_{22}H_{37}NO$: C 79.8; H 11.2;N 4.2).

The morpholinethiocarboxamide of (+)-*2-methylpentadecanoic acid* (*13*) was prepared according to the method described by Djerassi *et al.*[7] M.p. 110—112° (from cyclohexane). Rotatory dispersion in methanol $[\alpha]^{20}$: + 30° (650) mμ), + 32° (589 mμ), + 153° (373 mμ), —178° (328 mμ), —178° (310 mμ). *c* 0.05625, *l* 0.10 (307—348 mμ); *c* 0.1125, *l* 0.10 (310—400 mμ); *c* 0.1125, *l* 0.50 (372—650 mμ). (Found C 65.1; H 10.4; N 7.0. Calc for $C_{21}H_{40}N_2O_2S$ C 65.5; H 10.4; N 7.3).

(+)-*2L-Methylpentadecanoic acid* (*11*). A mixture of (—)-methyl 3-carboxy-2L-methylpropanoate [3,4] (2.1 g) and tridecanoic acid (6.2 g) in methanol containing sodium methoxide (from 0.1 g sodium) was electrolysed between platinum electrodes. The product was dissolved in light petroleum, the acidic material removed and the solvent evaporated. Hydrolysis by boiling with potassium hydroxide (6 g) in dioxan (250 ml) and water (20 ml) for 1 h gave a mixture of acids (1.5 g) which was chromatographed on silica gel (30 g) furnishing (+)-2L-methylpentadecanoic acid (1.0 g, 28 %), m.p. 39.5—41.5° (from light petroleum at —70°, followed by sublimation), $[\alpha]_D^{20}$ + 11.0° ($CHCl_3$, *c* 2.55). (Found: C 74.6; H 12.3; equiv. wt. 252. Calc. for $C_{16}H_{32}O_2$: C 75.0, H 12.5; equiv.wt. 256).

The anilide of (+)-*2L-methylpentadecanoic acid* (*12*) was prepared as described above. M.p. 96—96.5°, $[\alpha]^{20}$ + 22.4° ($CHCl_3$, *c* 3.08). (Found: C 79.2; H 11.0; N 4.6. Calc. for $C_{22}H_{37}NO$: C 79.8; H 11.2; N 4.2).

(+)-*Methyl 3-carboxy-2-dodecylbutyrate* (*16*). Dimethyl roccellate (*15*; 29 g) in a mixture of dioxan (625 ml) and 1,2-dimethoxyethane (250 ml) was refluxed for 1 h with aqueous sodium hydroxide (3.6 g in 250 ml of water). During the hydrolysis more water (60 ml) was added to keep the mixture homogeneous. The alkali soluble part was isolated in the usual way and washed repeatedly with boiling light petroleum (40—60°). The residue was fairly pure roccellic acid (7.5 g). The light petroleum extracts gave impure monoester (18 g, 65 %), m.p. 51—55°. Chromatography on silica gel (250 g) gave (+)-methyl 3-carboxy-2-dodecylbutyrate (13.5 g, 49 %), m.p. 56—58°, $[\alpha]_D^{20}$ + 11.8° ($CHCl_3$,

c 5.52). (Found: C 69.0; H 10.9; equiv.wt. 315. Calc. for $C_{18}H_{34}O_4$: C 68.8; H 10.8; equiv.wt. 314).

(+)-*Methyl 3-bromo-2-dodecylbutyrate* (*17*). Hunsdiecker degradation of the monoester (*16*; 11.0 g) gave (+)-methyl 3-bromo-2-dodecylbutyrate (10.2 g, 83 %), b.p. 147—148° (0.9 mm), $[\alpha]_D^{20}$ + 9.0° ($CHCl_3$, *c* 4.05), d_4^{20} 1.089. (Found: Br 22.6. Calc. for $C_{17}H_{33}BrO_2$: Br 22.9).

(+)-*Methyl 2-ethyltetradecanoate* (18). Debromination of the bromoester (17; 9.7 g) with zinc-acetic acid gave (+)-methyl 2-ethyltetradecanoate (6.9 g, 92 %), b.p. 116° (0.06 mm), $[\alpha]_D^{20}$ + 8.46° (undiluted, *l* 0.5), $[\alpha]_D^{20}$ + 9.2° ($CHCl_3$, *c* 12.93), d_4^{20} 0.858. The purity was proved by gas chromatography. (Found: Saponif. equiv. 266. Calc. for $C_{17}H_{34}O_2$: Saponif. equiv. 270).

(+)-*2-Ethyltetradecanoic acid* (*19*). The ester (*18*; 4 g) was refluxed for 45 min with a mixture of ethanol (250 ml) and aqueous sodium hydroxide (2 N, 75 ml). The product was chromatographed on silica gel (80 g), giving (+)-2-ethyltetradecanoic acid (3.2 g, 84 %), m.p. 24—27° or 28—30° (dimorphous), $[\alpha]_D^{20}$ + 7.0 ($CHCl_3$, *c* 14.60). On admixture with a synthetic sample, m.p. 24—26°, $[\alpha]_D^{20}$ + 5.2°, the melting point of the high melting modification was depressed to 25—27°. However, the infra-red spectra were identical and a mixture of (+)-2-ethyltetradecanoic acid (0.050 g) from roccellic acid and (−)-2D-ethyltetradecanoic acid (0.010 g) was shown to be identical with the synthetic (+)-2L-ethyltetradecanoic acid by means of rotation, melting point and mixed melting point. (Found: C 75.0; H 12.1, equiv.wt. 259. Calc. for $C_{16}H_{32}O_2$: C 75.0; H 12.5; equiv.wt. 256).

The anilide of (+)-*2-ethyltetradecanoic acid* (*20*) prepared as described above for the isomer (*12*) had m.p. 91—92.5° (from methanol), $[\alpha]_D^{20}$ + 12.2° ($CHCl_3$, *c* 1.81). Apart from a higher rotation this compound was identical with a synthetic sample as shown by means of mixed melting point determination and infra-red absorption. (Found: C 79.7; H 11.45; N 4.2. Calc. for $C_{22}H_{37}NO$: C 79.8; H 11.2; N 4.2).

The morpholinethiocarboxamide of (+)-*2-ethyltetradecanoic acid* (*21*) was prepared according to the procedure described by Djerassi *et al.*[7] M.p. 102—108° and 107—109° (dimorphous), $[\alpha]_D^{20}$ + 9.2° ($CHCl_3$, *c* 2.20), Rotatory dispersion in methanol $[\alpha]^{25}$: + 30° (360 mμ), 0° (500—525 mμ), −12° (600 mμ). *c* 0.0262, *l* 0.50 (350—375 mμ); *c* 0.131, *l a* 0.50 (375—600 mμ). (Found: C 65.3; H 10.8; N 7.0. Calc. for $C_{21}H_{40}N_2O_2S$: C 65.6; H 10.4; N 7.3).

Diethyl allylethylmalonate. Diethyl allylmalonate (300 g) was slowly added to a suspension of sodium hydride (48 % "in oil", 77 g) in a mixture of dioxan (1 l) and 1,2-dimethoxyethane (0.5 l). When the hydrogen evolution had ceased, ethyl iodide (250 g) was added in one protion. The resulting solution was left at room temperature overnight and then refluxed for 1 h. Most of the solvent (1 l) was evaporated and the product isolated in the usual way. The diethyl allylethylmalonate (270 g, 72 %) had b.p. 147—150° (85 mm), lit. 233° [8], 93—95°/0.5 mm [9].

Ethyl 2-carboxy-2-ethylpent-4-enoate. Sodium hydroxide (67 g) in dry ethanol (0.5 l) was added to a solution of diethyl allylethylmalonate (270 g) in dry ethanol (0.5 l). After standing overnight, the mixture was refluxed for 1 h. Acidic and neutral materials were separated by bicarbonate extraction, giving ethyl 2-carboxy-2-ethylpent-4-enoate (154 g, 88 % based on reacted material), which was used without further purification. In addition some unreacted starting material (75 g) was isolated. (Found: Equiv.wt. 195. Calc. for $C_{10}H_{16}O_4$: equiv.wt. 200).

Ethyl 2-ethylpent-4-enoate. Ethyl 2-carboxy-2-ethylpent-4-enoate (154 g) was added from a dropping funnel to high boiling mineral oil heated to 195° at reduced pressure (100 mm), allowing the decarboxylation product to distill off continuously. Redistillation gave ethyl 2-ethylpent-4-enoate (100 g, 83 %) b.p. 165—168°. (Found: Saponif. equiv. 152. Calc. for $C_9H_{16}O_2$: saponif. equiv. 156).

2-Ethylpent-4-enoic acid. Ethyl 2-ethylpent-4-enoate (100 g) was hydrolysed with sodium hydroxide in aqueous ethanol (1 N) giving 2-ethylpent-4-enoic acid (75 g, 98 %), b.p. 104—106° (12 mm, lit.[8] 208°). (Found: C 65.0; H 9.3; equiv.wt. 125. Calc. for $C_7H_{12}O_2$: C 65.6; H 9.4; equiv.wt. 128).

The S-Benzylthiuronium salt of 2-ethylpent-4-enoic acid prepared in the usual way had. m.p. 135.5—137.5°. (Found: C 61.1; H 7.35; N 9.75. Calc. for $C_{15}H_{22}N_2O_2S$: C 61.2; H 7.5; N 9.5).

(—)-*2L-Ethylpent-4-enoic acid.* The salt from 2-ethylpent-4-enoic acid (75 g) and quinine (190 g) was recrystallised eight times from successively smaller amounts of acetone (0.8—0.2 l). The quinine salt was decomposed with dilute hydrochloric acid giving (—)-2L-ethylpent-4-enoic acid (12 g, 16 %), b.p. 90.5—93° (0.5 mm), $[\alpha]_D^{20}$ —2.40° (undiluted, *l* 0.5), $[\alpha]_D^{20}$ —2.8° ($CHCl_3$, *c* 6.20), d_4^{20} 0.963. The configuration was established by degradation to (—)-2L-ethylsuccinic acid as described below.

(—)-*Methyl 3-carboxy-2L-ethylpropanoate* (*22*). (—)-2L-Ethylpent-4-enoic acid (9 g) was methylated with diazomethane. The methyl ester was dissolved in acetone (200 ml), the solution cooled in an ice-salt bath and potassium permanganate (27 g) added over a period of 5 h. The cooling bath was removed and the mixture was left overnight. The precipitate was then filtered off and washed with water containing sodium pyrosulfite. The combined washings were acidified and extracted with ether. Evaporation of the solvent and chromatography on silica gel gave (—)-methyl 3-carboxy-2L-ethylpropanoate (5.1 g, 45 %), b.p. 86—88°/0.05 mm, $[\alpha]_D^{20}$ —9.10° (undiluted, *l* 0.5), $[\alpha]_D^{20}$ —7.36° ($CHCl_3$, *c* 6.79), d_4^{20} 1.119. (Found: C 52.1; H 7.4; equiv.wt. 160; saponif.equiv. 168. Calc. for $C_7H_{12}O_4$: C 52·5; H 7.5; equiv.wt. 160; saponif.equiv. 160).

The S-Benzylthiuronium salt of (—)-*methyl 3-carboxy-2L-ethylpropanoate* was prepared n the usual way from the acid. M.p. 159—162°. (Found: N 8.6. Calc. for $C_{15}H_{22}N_2O_4S$: N 8.6).

(—)-*2L-Ethylsuccinic acid.* (—)-Methyl 3-carboxy-2L-ethylpropanoate (0.3 g) was hydrolysed with 0.5 N sodium hydroxide. The product was sublimed, then dissolved in water and the solution evaporated at room temperature. Crystallisation from benzene gave partially resolved (—)-2L-succinic acid (0.1 g), m.p. 93—95°, $[\alpha]_D^{20}$ —11.5° (H_2O, *c* 5.71). For the pure L-form Berner *et al.*[10] give m.p. 96°, $[\alpha]_D^{20}$ —18.5° (*cf.* Refs.[11,12]).

(+)-*2L-Ethyltetradecanoic acid* (*19*). A mixture of (—)-methyl 3-carboxy-2L-ethylpropanoate (*22*; 1.2 g) and lauric acid (4 g) in methanol containing sodium methoxide (from 0.1 g sodium) was electrolysed between platinum electrodes. The neutral part of the product was refluxed for 3 h with potassium hydroxide (5 g) in dioxan-water (10:1, 500 ml) to give docosane (1.9 g) and a mixture of acids (0.25 g). The acid fraction was repeatedly wased with light petroleum to give a residue of (—)-2L,5D-diethyladipic acid (0.01 g), m.p. 133—136°. The combined light petroleum extracts were chromatographed on silica gel. The main fraction (0.15 g) was washed with light petroleum at —70° and then sublimed, giving partially resolved (+)-2L-ethyltetradecanoic acid (0.10 g, 5.2 %), m.p. 24—26°, $[\alpha]_D^{20}$ + 5.2° ($CHCl_3$, *c* 2.06). (Found: C 74.5; H 12.4; equiv.wt. 253. Calc. for $C_{16}H_{32}O_2$: C 75.0; H 12.5; equiv. wt. 256.

The anilide of (+)-*2L-tetradecanoic acid* (*20*), prepared from a synthetic sample had m.p. 90—92° (from methanol, then from cyclohexane), $[\alpha]_D^{20}$ + 9.5° ($CHCl_3$, *c* 1.05). (Found: C 79.7; H 11.2; N 4.4. Calc. for $C_{22}H_{37}N$ O: C 79.8; H 11.2; 4.2).

(+)-*2L,5D-diethyladipic acid.* (—)-Methyl 3-carboxy-2L-ethylpropanoate (0.10 g) in methanol containing a trance of sodium methoxide, was electrolysed between platinum electrodes. Hydrolysis ofthe neutral part of the product gave (+)-2L,5D-diethyladipic acid (0.025 g, 36 %) m.p. 134—136° (from chloroform) $[\alpha]_D^{20}$ + 8.6° (EtOH, *c* 1.08). Lit m.p. 136°[13] and 136—136.6°[14] for the high melting optically inactive form of 2,5-diethyladipic acid. (Found: C 59.7; H 8.9; equiv. wt. 99. Calc. for $C_{10}H_{18}O_4$: C 59.4; H 8.9; equiv. wt. 101).

(+)-*2D-Ethylpent-4-enoic acid.* The mother liquiors from the preparation of the quinine salt of (—)-2L-ethylpentenoic acid were concentrated and subjected to further crystallisation. Evaporation of the solvent from the most soluble part and subsequent decomposition of the quinine salt with hydrochloric acid yielded (+)-2D-ethylpent-4-enoic acid (15.5 g, 21 %), b.p. 110—112°/13 mm, $[\alpha]_D^{20}$ + 2.0° (unidluted, *l* 0.5), d_4^{20} 0.962.

(+)-*Methyl 3-carboxy-2D-ethylpropanoate.* (+)-2D-Ethylpent-4-enoic acid (15.5 g) was methylated with diazomethane and then oxidized with potassium permanganate

in acetone. The product was chromatographed oh silica gel giving (+)-methyl 3-carboxy-2D-ethylpropanoate (6.9 g, 36 %), b.p. 141—142°/12 mm, $[\alpha]_D^{20}$ + 8.0° (undiluted, *l* 0.5), d^{20} 1.118.

(+)-*Dimethyl 2D-ethylsuccinate.* (+)-Methyl 3-carboxy-2D-ethylpropanoate was methylated with diazomethane furnishing (+)-dimethyl 2D-ethylsuccinate, b.p. 99°/14 mm $[\alpha]_D^{20}$ + 7.92 (undiluted, *l* 0.5) d_4^{20} 1.041. Berner [10] gives $[\alpha]_D^{20}$ −14.89° for the pure (−)-form.

(−)-*2D-Ethyltetradecanoic acid.* A mixture of (+)-methyl 3-carboxy-2D-ethylpropanoate (1.30 g) and lauric acid (3.3 g) in methanol was electrolysed between platinum electrodes. The neutral part of the product was distilled, giving four fractions, I (0.08 g), b.p. 65—70°/1 mm, $[\alpha]_D^{20} \sim 0$ ($CHCl_3$, *c* 7.0); II (0.25 g), b.p. 102—110°/1 mm, $[\alpha]_D^{20}$ −5.2° ($CHCl_3$, *c* 21.4); III (0.65 g), b.p. 110—120°, $[\alpha]_D^{20}$ −4.2° ($CHCl_3$, *c* 20.6), and IV (0.85 g), b.p. 140—160°/1 mm. From infra-red measurements it was clear that fraction (II) consisted partly of dimethyl 2D,5L-diethyladipate and fraction (IV) mainly of docosane. Fraction (III) was hydrolysed and chromatographed to give (−)-2D-ethyltetradecanoic acid (0.40 g, 20 %), m.p. 24—26°, $[\alpha]_D^{20}$ −4.2° ($CHCl_3$, *c* 8.50).

(−)-*2D,5L-Diethyladipic acid.* Dimethyl 2D,5L-diethyladipate from mixed electrolysis of (+)-methyl 3-carboxy-2D-ethylpropanoate and lauric acid (fraction II above) was hydrolysed with sodium hydroxide (0.5 N in ethanol-water 1:1), giving 2D,5L-diethyladipic acid (0.08 g, 10 %), m.p. 134—136° (from chloroform), $[\alpha]_D^{20}$ −7.8° ($CHCl_3$, *c* 2.70).

Acknowledgements. The author would like to thank Professor H. Erdtman and Tekn.-lic. B. Carnmalm for their interest in this work and for valuable discussions. The author is further indebted to Professor C. Djerassi and Miss A. M. Weidler for rotatory dispersion measurements and for a discussion of the results. Thanks are also due to Mr. E. Pettersson for technical assistance, to Miss G. Hammarberg for the infra-red measurements and to Dr. P. Daniels for checking the English.

Financial support form the *Swedish Technical Research Council* is gratefully acknowledged.

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Received September 15, 1961.