Sie lässt sich aus Nitromethan oder Toluol umkristallisieren. Zersp. 81—83°. Sintert bei etwa 70°. Rohausbeute 43 %. *Decylborsäure* ist fast unlöslich in Wasser und Lauge. Sie wurde aus Nitromethan-Äthylacetat (1:1) umkristallisiert. Zersp. 76—78°. Ausbeute 44 %. ($C_{10}H_{23}O_2B$ (186,1): Ber. C 64,54; H 12,46. Gef. C 64,82; H 13,07).

Bei der Darstellung der *Lauryl-*, *Myristyl-*, *Cetyl-* und *Stearyl*-borsäuren wurden den Vorschriften für *Oktylborsäure* bis auf die Aufarbeitung des Reaktionsguts gefolgt. Wegen der Schwerlöslichkeit der Produkte in Wasser ist es nicht notwendig die wässrige Schicht mit Äther zu extrahieren.

Laurylborsäure. Die bei der Aufarbeitung erhaltene ätherische Schicht wurde einige Stunden in den Kühlschrank gestellt, um den gebildeten Kohlenwasserstoff möglichst zum Ausfällen zu bringen, wonach dieser abfiltriert wurde. Diese Fraktion bestand aus fast reinem Tetrakosan. Schmp. 56,0—56,5°. ($C_{24}H_{50}$(338,6) Ber. C 85,12; H 14,88. Gef. C 84,70; H 15,23). Die Ätherlösung wurde dann wie oben eingedampft. Der Niederschlag wurde wiederholt aus Toluol umkristallisiert, wobei die Lösung nur auf Zimmertemperatur gekühlt wurde, um Mitfällung von Kohlenwasserstoff zu vermeiden. Zersp. 70—75°. ($C_{12}H_{27}O_2B$(214,2): Ber. C 67,30; H 12,71. Gef.C 68,03; H 12,54). Die Ausbeute war gering.

Myristylborsäure wurde ähnlich wie Laurylborsäure dargestellt. Ausbeute 24 %. Zersp. 74—76°. ($C_{14}H_{31}O_2B$ (242,2): Ber. C 69,41; H 12,90. Gef. C 70,38; H 12,89).

Cetylborsäure. Es wurde von 20 g Cetylbromid + 1,9 g Magnesium in 90 ml Äther und 18 g Tributylborat in 40 ml Äther ausgegangen. Die bei der Hydrolyse gewonnene Ätherlösung wurde über Nacht sich selbst überlassen. Nach Abfiltrieren des Niederschlags (Dotriakontan) wurde die Lösung einige Stunden auf —10° abgekühlt. Die gebildeten Kristalle, 3 g, die etwas mit Kohlenwasserstoff verunreinigt waren, wurden wiederholt aus Toluol umkristallisiert. Beim Eindampfen der Ätherlösung konnte noch etwas von der Substanz erhalten werden. Zersp. 78—79°. ($C_{16}H_{35}O_2B$ (270,3): Ber. C 71,08; H 13,06. Gef. C 72,52; H 13,38).

Stearylborsäure wurde aus Stearylmagnesiumbromid und Tributylborat nach den Vorschriften für Oktyl- und Cetylborsäure dargestellt. Ausbeute 33 %. Zersp. 82—84°. ($C_{18}H_{39}O_2B$ (298,3): Ber. C 72,51; H 13,18. Gef. C 73,45; H 13,41).

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Synthesis of the *cis*- and *trans*-Isomers of Methyl 2,4L,21,21-tetramethyl- L$\Delta^{2:3}$-docosenoate

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In the course of work on the synthesis of compounds structurally related to C_{27}-phthienoic acid from virulent tubercle bacilli [1], Ställberg-Stenhagen [2] prepared the *trans*-isomer of 2,4D-dimethyl-$\Delta^{2:3}$-heneicosenoic acid. This acid and its ethyl ester were strongly laevorotatory. The corresponding *cis*-compound and the isomer with α-methylene structure were not isolated in pure form, but both appeared to be dextrorotatory.

The *cis*- and *trans*-isomers of methyl 2,4L,21,21-tetramethyl-$\Delta^{2:3}$-docosenoate have now been prepared in order to study the biological properties of fatty acids related to the phthienoic acid type but possessing a neopentyl group in ω-position, the presence of which renders biological ω-oxidation difficult. The *trans*-ester is strongly dextrorotatory, whereas the *cis*-ester is laevorotatory, the molecular rotations being +69° and −40°, respectively. The geometrical arrangement of the substituent groups attached to the carbon atoms forming the α,β-double bond has thus a very marked effect on the optical rotation of the asymmetric carbon atom in γ-position.

The synthesis follows that of racemic methyl phthienoate described by Asselineau *et al.*[3]

Experimental. Methyl 17,17-dimethyloctadecanoate was prepared from *tert*-butylacetic acid and methyl hydrogen tetradecane-1,14-dioate *via* the Kolbe reaction. Hydrolysis gave

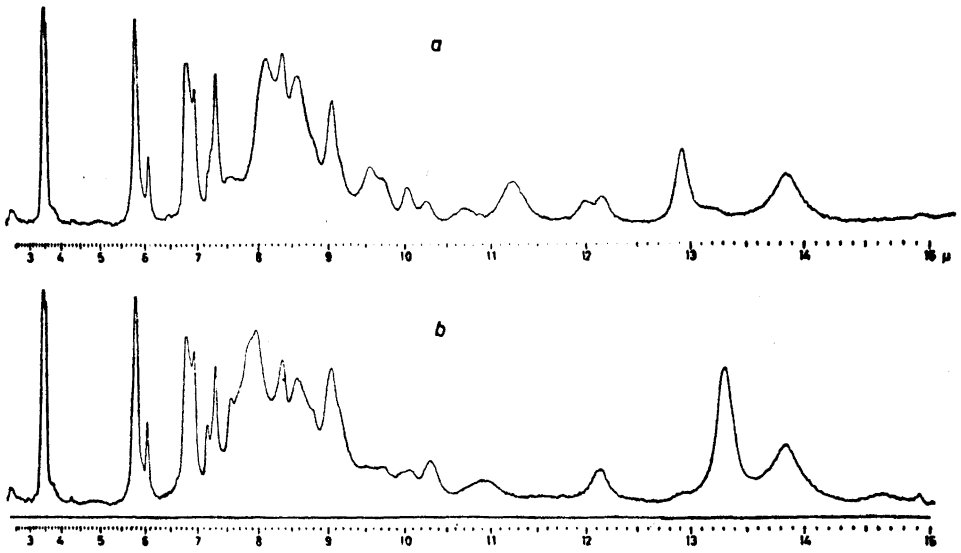

Fig. 1. Infra-red absorption spectra in the liquid state: a) (—)-methyl *cis*-2,4L,21,21 tetramethyl-$\Delta^{2:3}$-docosenoate; b) (+)-methyl *trans*-2,4L,21,21-tetramethyl-$\Delta^{2:3}$-docosenoate Cell thickness 0.02 mm.

17,17-dimethyloctadecanoic acid of m. p. 56.7 —57.2° (Sobotka and Stynler [4] give m. p. 57.2 —57.7°), which, *via* a second mixed Kolbe reaction with (—)-methyl hydrogen β-methylglutarate [5], followed by hydrolysis, gave (—)-3L, 20,20-trimethylheneicosanoic acid (m. p. 43.5—43.9°, $[M]_D^{27}$ — 12.6° (chloroform; *c*, 14.5), amide m. p. 91.7—91.9°). Reaction of the acid chloride of this acid with methyl cadmium [6] gave (—)-2-oxo-4L, 21,21-trimethyldocosane. After purification by chromatography on aluminium oxide the ketone had n_D^{30} 1.4477, $[\alpha]_D^{22}$ — 4.6° (chloroform, *c*, 10.4). It was converted into cyanhydrin by means of hydrogen cyanide, and the crude cyanhydrin was hydrolysed by hydrochloric acid in glacial acetic acid to a mixture of stereoisomeric hydroxy-acids melting at 83.8—85.1°. This mixture was pyrolysed by heating to 206° for one hour, followed by half an hour at 215°. After treatment with diazomethane in ether solution the resulting mixture of methyl esters was separated by chromatography on aluminium oxide. (—)-Methyl *cis*-2,4L,21,21-tetramethyl-$\Delta^{2:3}$-docosenoate, m.p. 25.5—25.8°; n_D^{25} 1.4572; $d_4^{24.5}$ 0.869; $[\alpha]_D^{24.5}$ —9.87° ± 0.27° (chloroform; *c*, 7.6); $[M]_D^{24.5}$ —40°, was followed by (+)-methyl *trans*-2,4L, 21,21-tetramethyl- $\Delta^{2:3}$ -decosenoate, m. p. 27.1—27.5°, n_D^{25} 1.4588 (supercooled liquid); $[\alpha]_D^{26}$ + 16.9° ± 1.0° (chloroform; *c*, 1.95); $[M]_D^{26}$ + 69°. Ultra-violet spectrum: *cis*-isomer λ_{max} 216 mμ, ε = 10.200; *trans*-isomer λ_{max} 215 mμ, ε = 13.500 (hexane).

The infra-red spectra are shown in Fig. 1. The strong absorption band at 750 cm^{-1} (13.33 μ) of the *trans*-isomer is observed also in the spectra of racemic methyl phthienoate [2] and methyl *trans*-2,4D-dimethyl-$\Delta^{2:3}$-heneicosenoate [2], and thus appears characteristic for methyl esters of acids having the 2,4-diMe-2-enoic structure. In methyl *trans*-2,5D-dimethyl-$\Delta^{2:3}$-heneicosenoate the frequency is shifted to 740 cm^{-1} (13.51 μ).

In the spectra of *cis*-forms of the 2,4-diMe-2-enoate structure, represented by the *cis*-ester now described and by the *cis*-isomer of racemic methyl phthienoate, a corresponding absorption occurs at 773 cm^{-1} (12.93 μ).

Details of this work will be published later.

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On the Effect of Organic Mercury Compounds and Copper Salts on Catalase Cyanide

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In connection with studies of different antidotes in cyanide poisoning it became of interest to investigate the action of certain heavy metal compounds on cyanide inhibited heme enzymes. The toxicity of cyanide is attributed to its inhibitory action on cytochrome oxidase, but another heme enzyme, catalase, was used as a model enzyme in these studies, as it in contrast to cytochrome oxidase can be obtained in a pure state. It is of importance in this connection that catalase qualitatively behaves as cytochrome oxidase in its reaction with cyanide, as both the association and dissociation velocity constants are high [1]. It has previously been demonstrated by Chance [1] that silver ions generate free catalase from the catalase cyanide complex, due to the fact that silver ions combine with the free cyanide in equilibrium with catalase cyanide. The high toxicity of silver salts, however, apparently prevents their use as antidotes in cyanide poisoning. Incidentally we observed that organic mercury compounds had a high affinity for cyanide and could completely reactivate cyanide inhibited catalase. This suggested that these compounds may have an antidotal effect in cyanide poisoning. Of special interest were those organic mercury compounds which are used as diuretics, as they might be easily available for use as antidotes. The complete reactivation of cyanide inhibited catalase by one of these diuretics, Mersalyl (Salyrgan), is shown in Fig. 1. Experiments on rabbits [2] demonstrated, however, that Mersalyl had no antidotal effect in cyanide poisoning. Presumably the mercury compound was bound to sulfhydryl groups in the body before it could react with cyanide. (The mercurials have a very high affinity for sulfhydryl groups and their diuretic action is in fact attributed to an inhibition of sulfhydryl enzymes in the kidney.)

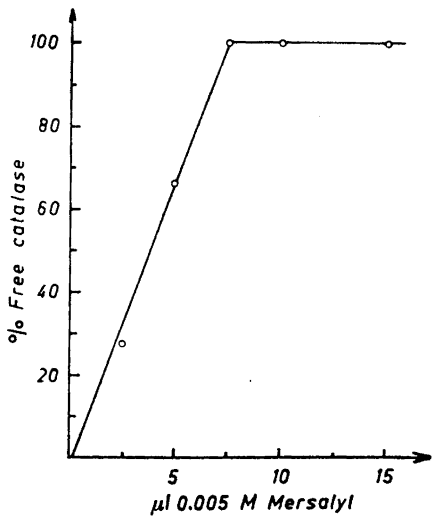

Fig. 1. Effect of Mersalyl on catalase cyanide. Horse blood catalase 0.8×10^{-6} M, cyanide 1×10^{-5} M, phosphate buffer 0.025 M of pH 7.4, final volume 3.0 ml. Indicated amounts of the mercurial added and the free catalase formed was determined spectrophotometrically from the decrease in absorbancy at 425 mµ.

Agner [3] reported that cupric salts could be used as antidotes in cyanide poisoning. This was disputed by Walther and Meyer [4] but Agner's results have been confirmed in connection with the present work [5]. However, when the effect of cupric chloride on catalase cyanide was studied, it was found that even a considerable excess of cupric