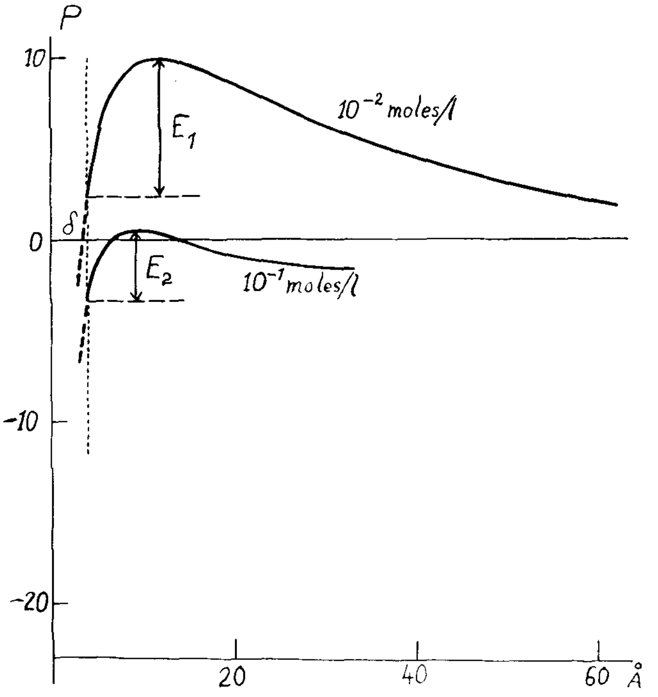

FIG. 4. Energy barriers E_1 and E_2 at electrolyte concentrations $c = 10^{-2}$ and 10^{-1} moles/l., respectively, for $\psi_0 = 100$ mV.

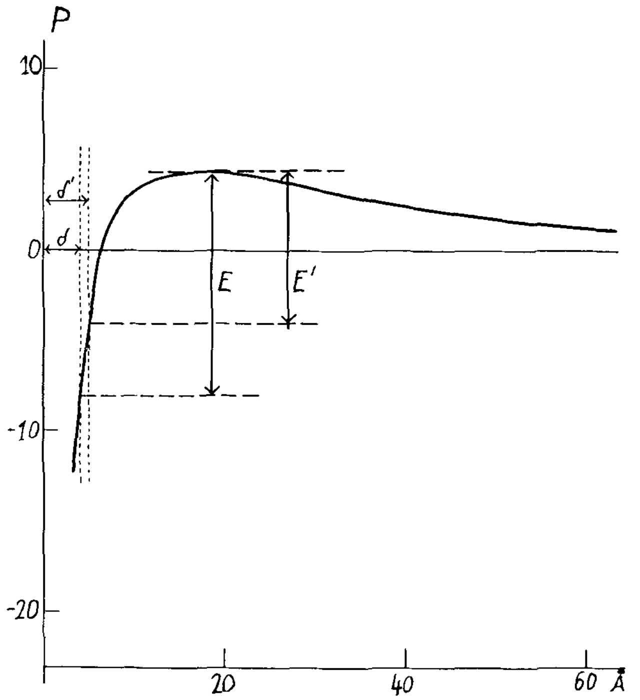

FIG. 5. Energy barriers E and E′ for minimum distances of $\delta = 4$ Å and $\delta' = 5$ Å, respectively, $\psi_0 = 75$ mV, $c = 10^{-2}$ moles/l.

sults in an enlargement of the minimum distance and, as a consequence, in a reduction of the energy barrier the soil particle has to surpass when moving away from the fiber (Figure 5).

For a further development of the theory, certain refinements are necessary, which can only be mentioned but not explained. For example, the fact that the interfacial potentials on the fiber and on the soil usually have different values has to be allowed for. The theory of dispersion forces proposed by London (11) must be modified by recent theories of Casimer and Polder (2) as well as by those of Lifschitz (10). Some corrections of the Gouy-Chapman theory of the electric double layer should be applied. Finally it will be necessary to investigate the properties of the hydration shells, the influence of which has been expressed provisionally by the term δ. Such investigations have been started by recent work (9) concerned with the influence of detergents on the stability of hydrophobic sols at high ionic strength.

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Preparation of 8t,10t-Octadecadienoic Acid[1]

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SMIT (1) ISOLATED a conjugated linoleic acid (m.p. 56°) by debromination of a tetrabromostearic acid, which had a melting point of 124°. The latter was isolated by them from the brominated products obtained by brominating the distillate of the fatty acid from castor oil. They assigned a structure of 9,11-octadecadienoic acid to this fatty acid and believed it to be elaidinized.

von Mikush (2) distilled the fatty acids obtained from castor oil according to the method of Scheiber (3) and brominated the distilled fatty acids in petroleum ether at −20°. From the bromination product he isolated tetrabromostearic acids of different melting points. Upon debromination of one of these tetrabromostearic acids (m.p. 124°) with zinc in ethanol and by crystallization of the resultant product from aqueous ethanol, he isolated an acid which melted at 55.5–56.5°. This acid was assigned a *trans-trans* structure on the basis of diene and pentadiene values and

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a structure of 8,10-octadecadienoic acid, as suberic acid could be isolated from its permanganate oxidation products. Schmidt and Lehmann (4) prepared 9,11-octadecadienoic acid (m.p. 32–33°) by allylic bromination of methyl oleate, followed by dehydrobromination and hydrolysis of the resultant ester. Grigor *et al.* (5) prepared another geometrical isomer of 9,11-octadecadienoic acid (m.p. 53–54°) by reacting methyl ricinoleate with thionyl chloride, followed by dehydrochlorination and hydrolysis of the crude halogenated product (methyl 12-chloro-9-octadecenoate) with alcoholic potassium hydroxide.

Sparreboom (6) has recently reported the synthesis of *cis,cis*-9,11-, and *cis,cis*-10,12-octadecadienoic acids, melting at 42.0–43.2° and 38.2–39.0°, respectively, by coupling 1-octyne with 9-decynoic acid and 1-heptyne with 10-undecynoic acid in the presence of cuprous ammonium chloride. In order to obtain the dienoic acids, he isolated the pure acetylenic acids and partially hydrogenated them in the presence of Lindlar catalyst and quinoline in alcohol.

In the present communication we report a method for the preparation of 8t,10t-octadecadienoic acid (m.p. 56–56.5°) in 15–20% yield and the isolation of a little of 9,11-octadecadienoic acid, melting at 33–34°. *Trans,trans*-8,10-octadecadienoic acid was prepared by allylic bromination of oleic acid with N-bromosuccinimide in carbon tetrachloride in the presence of benzoyl peroxide (7). The crude brominated product was isolated and further brominated by the addition of free bromine in ether at −10 to 0°. The ether was evaporated under vacuum, and the crude brominated product was debrominated by zinc in ethanol according to the procedure described by Rollett (8). The methyl esters were fractionally distilled and examined in the ultraviolet spectrum (Table I). The second, third, and fourth fractions were combined, and approximately 45 g. of the esters were hydrolyzed by refluxing with alcoholic potassium hydroxide, followed by acidification and extraction. Five g. of the resulting acids were crystallized from aqueous alcohol and from petroleum ether (40–60°); two acids melting at 33–34° and 37–42° were isolated. The former was examined in the ultraviolet spectrum, which indicated it to be a conjugated dienoic acid. It was probably the 9,11-octadecadienoic acid (m.p. 33–34°) reported by Schmidt and Lehmann (4). The acid melting at 37–42° could not be further purified by crystallization. The ultraviolet and infrared spectra data indicated the presence of conjugated dienoic acid.

TABLE I
Fractionation of Ethyl Esters Obtained Upon Debromination

Fraction No.	Boiling point (°C.) at 0.25–0.4 mm.	Weight of the fraction	Conjugated dienoic acid
		(g.)	*(%)*
1	140–142	2.5	25.5
2	148–150	15.8	74.2
3	150–154	25.4	75.6
4	154–160	10.3	75.3
5	Residue	12.2	......

Ten g. of the fatty acids were irradiated by ultraviolet light in petroleum ether in the presence of iodine for 3–4 hrs. Upon cooling and crystallization from petroleum ether 3.5 g. of an acid melting at 56–56.5° were obtained. The infrared spectral data indicated the presence of *trans-trans* conjugated double bonds. Upon reduction of the acid in ethyl acetate in the presence of platinum catalyst, stearic acid melting at 68–69° was obtained (mixed melting-point with an authentic sample, 68–69°). In order to establish the position of the double bonds, the acid was oxidized by permanganate in acetone and suberic acid melting at 139.5–140° was isolated (mixed melting-point with an authentic sample of suberic acid, 139.5–140.5°).

Experimental

Preparation of Oleic Acid. This acid was prepared from olive oil according to the procedure of Knight *et al.* (9) described in *Biological Preparations,* $n^{20/D}$ iodine value 58.2 (Wijs), bromine, 35.4%.

Bromination of Oleic Acid. The oleic acid was brominated in two stages; in the first stage it was brominated in both of its allylic positions by refluxing with N-bromosuccinimide in carbon tetrachloride, and in the second stage the brominated product was further brominated by the addition of free bromine to the double bond of the acid.

a) Ninety-four g. of oleic acid (0.33 mole), 300 ml. of dry carbon tetrachloride, 125.3 g. of N-bromosuccinimide (0.7 mole), and 0.1 g. of benzoyl peroxide were added to a 1-liter round-bottom flask, and the flask was connected to a reflux condenser protected with a calcium chloride tube. The material in the flask was refluxed on a steam bath for 12 hrs., then cooled in the refrigerator. The reaction product was filtered through a Büchner funnel to remove the succinimide. The solvent in the filtrate was removed under vacuum, 145.2 g. of a light brown viscous liquid were obtained, iodine value (Wijs) 58.2, bromine, 35.4%.

b) Approximately 132 g. of the brominated product were transferred to a 1-liter three-necked flask, fitted with a stirrer and a dropping funnel, and the brominated product was dissolved in 650 ml. ether. Approximately 48 g. of bromine were added slowly from the dropping funnel while the contents in the flask were stirred and the temperature was maintained between −10 and −5°. After the addition of bromine the material in the flask was allowed to warm to room temperature, and the solvent was removed under vacuum. Approximately 175 g. of a brown viscous liquid were obtained, iodine value (Wijs) 0.00, bromine 52.8%. The brominated product could not be crystallized.

Debromination. Approximately 150 g. of the brominated product obtained in (b) were debrominated with zinc in ethanol under an atmosphere of nitrogen (8); 72.3 g. of the ethyl esters were obtained, $n^{22/D}$ 1.4779, neutral. equiv. 311.2, iodine value (Wijs) 115.8, conjugated dienoic acids 51.1%, and conjugated trienoic acid 0.00%.

Fractional Distillation. Sixty-six and seven-tenths g. of the ethyl esters were fractionally distilled under vacuum (0.25–0.4 mm.). The boiling points, yields, and percentage of conjugated dienoic acids obtained are recorded in Table I.

Isolation of the 8t,10t-Octadecadienoic Acid. Since the second, third, and fourth fractions had a high content of conjugated dienoic acids, these fractions were combined for further work. Approximately 45 g. of the ethyl ester were hydrolyzed by refluxing with 200 ml. of N alcoholic potassium hydroxide, followed by acidification with dilute hydrochloric acid. The fatty acids were extracted with ether, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum; 42.3 g. of fatty acids were obtained. Approximately 5 g. of the fatty acids were recrystallized from aqueous alcohol, yield 2.8 g., m.p. 30–34°, and then from petroleum ether (40–60°), m.p. 37–42°. The melting point of the acid did not increase upon repeated crystallization, neutral. equiv. 282.2, conjugated dienoic acids 99.5%. The mother liquor was concentrated, and upon cooling an acid, m.p. 33–34°, was obtained. From the ultraviolet spectrum the presence of conjugated double bonds was indicated; this acid may be the 9,11-octadecadienoic acid reported by Schmidt and Lehmann (4).

In order to isolate 8t,10t-octadecadienoic acid, 10 g. of the fatty acids were dissolved in 30 ml. of petroleum ether (40–60°) and irradiated for 2–3 hrs. with ultraviolet light in the presence of traces of iodine. The solution was cooled and filtered; 5.2 g. of crystals, m.p. 44–48°, were obtained. Upon recrystallization from petroleum ether (40–60°), 3.8 g. of crystals, m.p. 56–56.5°, were obtained. From the infrared spectrum data, the configuration of the double bonds of the acid was indicated as conjugated *trans,trans*-dienoic acid. The presence of conjugated double bonds was further confirmed by ultraviolet spectrum data.

Anal. calc. for $C_{18}H_{32}O_2$: carbon, 77.14%; hydrogen, 11.42%.
Found: carbon, 77.09%; hydrogen, 11.47%.

Oxidation of 8t,10t-Octadecadienoic Acid with Potassium Permanganate in Acetone. One g. of the pure 8t,10t-octadecadienoic acid, m.p. 56–56.5°, was dissolved in dry acetone (25 ml.) in a 100-ml. round-bottomed flask. Approximately 4 g. of the powdered potassium permanganate were added slowly to the contents of the flask, which was cooled whenever necessary during the addition of potassium permanganate. The material in the flask was refluxed on a steam bath for about 2 hrs. The acetone was removed, and cold water was added to the flask. The material was acidified with dilute sulfuric acid, and excess permanganate was decolorized by sodium bisulfite. The contents in the flask were warmed until an almost clear solution was obtained. Upon cooling, the material was extracted with ether, washed with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the residue was extracted with hot water. The water extract was treated with activated charcoal and filtered. Upon cooling, suberic acid crystallized out. It was recrystallized from a mixture of benzene and petroleum ether (40–60°), m.p. 139.5–140°, mixed melting-point with an authentic sample of suberic acid, 139.5–140.5°.

Hydrogenation of 8t,10t-Octadecadienoic Acid. Two-tenths g. of acid was dissolved in 10 ml. of ethyl acetate and hydrogenated in the presence of platinum catalyst. The catalyst was filtered off, and the solvent was removed under vacuum. The residue was recrystallized from ethyl acetate, m.p. 68–69°, mixed melting-point with an authentic sample of stearic acid, m.p. 68–69°.

Summary

Oleic acid was brominated with N-bromosuccinimide, followed by addition of free bromine to the double bond. Upon debromination of the brominated product with zinc in ethanol and fractionation of the resultant ethyl esters, the fractions containing 74–75% of conjugated dienoic acids were combined. The ethyl esters were hydrolyzed; upon irradiation by ultraviolet light of the fatty acids in petroleum ether (40–60°) in the presence of a trace of iodine, and upon cooling, 8t,10t-octadecadienoic acid, m.p. 56–56.5°, was obtained in 15–20% yield.

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Octadecylsulfuric Acid. Properties of the Acid, Amine Salts, and Salts of Amino Acids[1]

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IN A CONTINUATION of previous work on tallow alcohol sulfates (9) it became of interest to prepare and isolate long-chain alkylsulfuric acids, in particular, octadecylsulfuric acid. The purpose was to study the stability and properties of the free acid and to make use of the acid in the rapid screening of a variety of salts for detergent and surface-active properties.

Only a few references are known which concern the preparation and description of long-chain alkylsulfuric acids. Dodecylsulfuric acid was prepared by Ross and co-workers (7) as a flaky, hygroscopic, crystalline mass, by sulfation of dodecanol with chlorosulfonic acid by using liquid sulfur dioxide as the solvent. Dodecyl- and hexadecylsulfuric acids were prepared by Desnuelle and co-workers (3) by acidification and extraction of aqueous solutions of the sodium salts. By the use of conditions which minimize or exclude moisture we have found a direct method

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