and the solution dried over anhydrous sodium sulfate. The yield of a gummy amorphous material was 2.93 g. (0.92%). Quantitative precipitation from petroleum ether with an equal volume of ethanol gave a powdery, light brown material. Paper strip chromatography according to the method of Bevan *et al.*[23] gave only one phospholipid spot which was negative to ninhydrin but indicative of a lecithin, according to its R_f value of 0.92. It gave a positive fuchsin-aldehyde test with mercuric acetate. The test was negative without the mercury salt. The infrared showed a strong carbonyl peak at 5.78 μ and the melting behavior was also typical of the lecithins with softening occurring at 90°, and meniscus formation at 210–220°. $[\alpha]_D^{24°} = +12.6°$ (1.11% in chloroform, $\alpha = +0.14°$).

Anal. Calcd. for $C_{48}H_{98}NO_8P$: P, 3.65; N, 1.65; choline, 14.3. Found: P, 3.65; N, 1.60; choline, 14.9. N:P:choline = 0.97:1:1.04.

The ether insoluble fraction had an infrared spectrum similar to the major phospholipid fraction. Its melting behavior was also similar.

Anal. Found: P, 1.05; N, 6.01. N:P = 12.6:1.

No further identification was attempted.

Quantitative hydrogenation of the plasmal lecithin. An 18.9-mg. sample of the phospholipid (23.9 μM) was dissolved in 8 ml. of *n*-butyl ether after the platinum catalyst (19 mg.) was reduced in the microhydrogenation apparatus.[26] At 22° and 754 mm., the sample required 1.04 ml. of hydrogen or 0.946 ml. at STP (42.2 μM). The number of double bonds was 1.77 per mole of phospholipid.

Alkaline hydrolysis of hydrogenated phospholipid. The compound (500 mg.) was dissolved in 75 ml. of *n*-butyl ether and hydrogenated over platinum in a Parr shaker for 21 hr. The catalyst was then filtered off and the solvent removed at 2 mm. and room temperature. The residue was dissolved in 30 ml. of ethyl ether and 30 ml. of 0.5*N* methanolic potassium hydroxide was added. This cloudy mixture was shaken in a stoppered flask at room temperature for 21 hr. Water (20 ml.) was then added and the mixture extracted twice with 25 ml. of ether. The ether extract was washed twice with 10 ml. of water and dried over sodium sulfate. The solvent was evaporated to yield an oil containing a white solid. The oil was removed by dissolving it in 10 ml. of ether leaving 30 mg. (17%) of the solid whose infrared spectrum was typical of a fatty acid salt.

Anal. Calcd. for $C_{18}H_{35}O_2K$: C, 67.08; H, 10.86. Found: C, 67.13; H, 10.45.

The alcoholic solution was filtered, acidified with 1 ml. of concd. hydrochloric acid, and extracted again with three 25-ml. portions of ether. The extract was washed twice with 10 ml. of water and dried. This solution of fatty acids was esterified with diazomethane distilled with the ether from a solution of 1.2 g. of *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide, slowly added to 30% ethanolic potassium hydroxide. The excess diazomethane was allowed to evaporate with the ether and the methyl esters remaining were combined with the ether soluble methyl esters first extracted from the alkaline hydrolysis mixture. The yield was 142 mg. (76%).

The material filtered from the alkaline hydrolysis mixture contained phosphorus. It was taken up in 2 ml. of chloroform and precipitated with 8 ml. of acetone. The precipitate was dissolved in 1 ml. each of pyridine and benzene and reprecipitated with 8 ml. of acetone. The dried powder had no carbonyl band in the infrared and had a strong hydroxyl peak typical of a glyceryl ether phosphate. The yield was 25 mg. (8%).

Anal. Calcd. for $C_{21}H_{43}O_6PK_2$: C, 50.40; H, 8.60. Found: C, 49.47; H, 8.83.

Acid hydrolysis. The lecithin (84 mg.) was dissolved in 1 ml. of chloroform, and 2 ml. of concd. hydrochloric acid and 8 ml. of ethanol were added. This mixture was allowed to stand over a few milligrams of mercuric acetate for 24 hr., after which time hydrolysis seemed complete, as the solution was almost clear. The solution was then filtered and extracted three times with 10 ml. of petroleum ether. The solvent was removed from the extract, the residual oil taken up in 2 ml. of ethanol and 2 ml. of 2,4-dinitrophenylhydrazine reagent added. A precipitate formed immediately but the mixture was refrigerated overnight. The 2,4-dinitrophenylhydrazones were centrifuged and dissolved in benzene. The benzene solution was passed through an alumina column to purify the 2,4-dinitrophenylhydrazones. The benzene was removed to yield a red oil which could not be successfully crystallized. The yield was 25 mg. (53%).

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

A Unique Fatty Acid from *Limnanthes douglasii* Seed Oil: The C_{22} Diene

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Received July 6, 1960

The C_{22} dienoic fatty acid of *Limnanthes douglasii* seed oil (representing 10% of the total fatty acid) is shown to be the previously unknown *cis*-5-*cis*-13-docosadienoic acid.

An earlier paper from this laboratory[2] reports that the major components of seed oil from *Limnanthes douglasii* are *cis*-5-eicosenoic, *cis*-5-docosenoic, *cis*-13-docosenoic acids, and a C_{22} acid of undetermined structure. This paper reports the isolation and characterization of the remaining component as a previously unknown docosadienoic acid.

Concentration of the docosadienoic acid. A concentrate of the C_{22} diene acid (I) was obtained by low temperature crystallization of mixed free acids from heptane and subsequent countercurrent distribution (Fig. 1 and Table I).

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(1) One of the laboratories of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

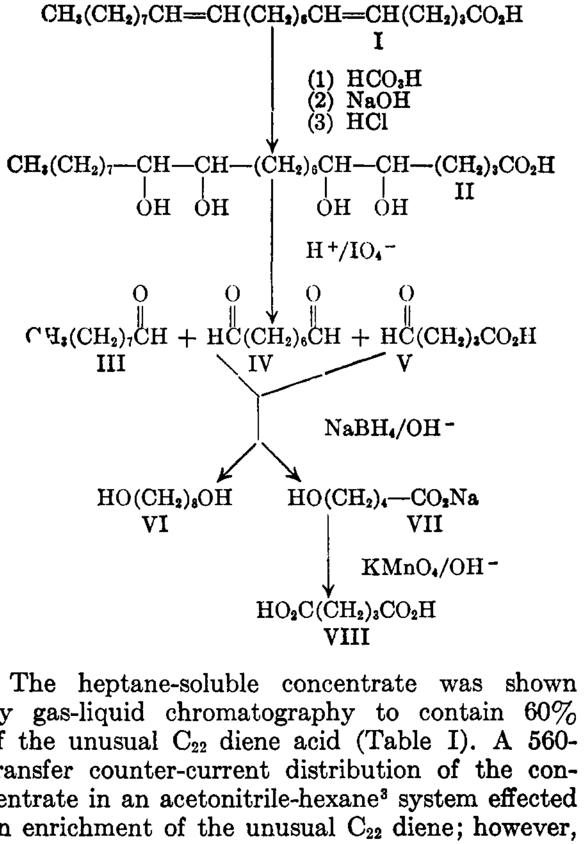
(2) C. R. Smith, Jr., M. O. Bagby, T. K. Miwa, R. L. Lohmar, and I. A. Wolff, presented before the Division of Organic Chemistry, 137th Meeting American Chemical Society, Cleveland, Ohio, April 5–14, 1960. C. R. Smith, Jr., M. O. Bagby, T. K. Miwa, R. L. Lohmar, and I. A. Wolff, *J. Org. Chem.*, 25,1770 (1960).

TABLE I

GAS CHROMATOGRAPHIC ANALYSIS OF METHYL ESTERS OF FRACTIONS DERIVED FROM *Limnanthes douglasii* FATTY ACIDS

	Equivalent Chain Length[a]		% Acid					
				Countercurrent Distribution (Transfer Number)				
Type of Acid	Apiezon-L	Resoflex-446	Heptane Soluble	310	330	350	390	336–394
C_{12} Saturated	12.0	12.0	0.1					
C_{14} Saturated	14.0	14.0	0.2					
C_{16} Saturated	16.0	16.0	1				0.8	0.1
C_{16} Monoene	15.7	16.4	2				—	—
C_{17} Saturated	17.0	17.0	0.5				—	—
C_{18} Saturated	18.0	18.0	—	—	0.5		—	0.1
C_{18} Monoene	17.7	18.4	7	0.3	0.2		3.1	0.5
C_{18} Diene	17.6	19.0	3					
C_{18} Triene	17.6	19.8	3					
C_{19} Unsaturated	18.7	—	—	—	—		1.3	0.2
C_{20} Saturated	20.0	20.0	—	0.6	—		—	—
C_{20} Monoene	19.7	20.4	13	7.3	34.5	19.7	0.7	17.2
C_{20} Unknown	19.4	20.6	3	0.2	—	—	—	1.6
C_{22} Monoene	21.7	22.4	5	72.3	9.6	—	—	—
C_{22} Diene[b]	21.6	23.0	1					
C_{22} Unknown (diene)	21.4	22.6	60	2.2	55.6	80.3	82.6	80.2
C_{24} Unknown	23.4	24.6	1	16.3	—	—	—	—

[a] According to T. K. Miwa, K. L. Mikolajczak, F. R. Earle, and I. A. Wolff, in a paper presented before the Division of Analytical Chemistry, 137th Meeting American Chemical Society, Cleveland, Ohio, April 5–14, 1960. T. K. Miwa, K. L. Mikolajczak, F. R. Earle, and I. A. Wolff, *Anal. Chem.*, **32**,1739 (1960). [b] This diene is not discussed in the text.



The heptane-soluble concentrate was shown by gas-liquid chromatography to contain 60% of the unusual C_{22} diene acid (Table I). A 560-transfer counter-current distribution of the concentrate in an acetonitrile-hexane[3] system effected an enrichment of the unusual C_{22} diene; however, the C_{20} monoene present was not resolved from the mixture (Table I). The C_{22} diene concentrate, of about 80% purity, was obtained by combining material from transfers 336 to 394 (Table I).

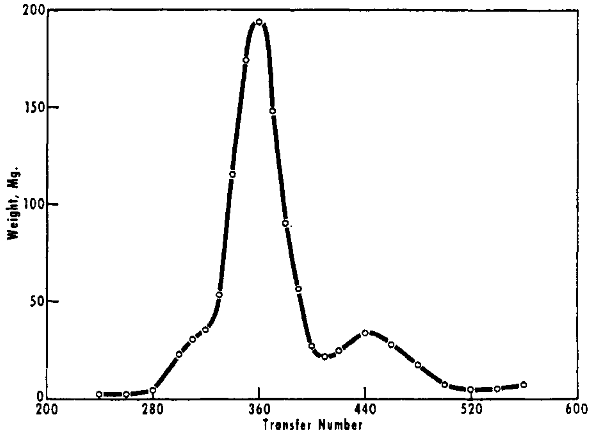


Fig. 1. Countercurrent distribution of heptane-soluble acids (−55°) from *Limnanthes douglasii* seed oil

The presence of two double bonds was confirmed by iodine value (Wijs) and quantitative hydrogenation; however, alkali isomerization[4] failed to yield appreciable (< 2%) conjugation. Treatment with lipoxidase[5] indicated no methylene interrupted *cis*-unsaturation.

The C_{22} acid was isolated by hydroxylating the concentrate with performic acid[6] and subsequent solvent extraction. The high yield of tetrahydroxy acid, contrasted to the low yields reported for the oxidation of linoleic acid,[6,7] was probably due to the greater separation of the double bonds.

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(3) C. R. Scholfield, J. Nowakowska, and H. J. Dutton, *J. Am. Oil Chemists' Soc.*, **37**, 27 (1960).

(4) American Oil Chemists' Society, *Official and Tentative Methods*, 2nd ed., revised 1959, Cd 7-58.

(5) J. MacGee, *Anal. Chem.*, **31**, 298 (1959).

(6) D. Swern and G. B. Dickel, *J. Am. Chem. Soc.*, **76**, 1957 (1954).

Characterization of tetrahydroxy acid. The purified tetrahydroxydocosanoic acid (II) was subjected to oxidative cleavage by acid-periodate.[8] The steam-volatile aldehyde (III) was isolated by extracting the aqueous aldehyde mixture with petroleum ether and subsequent steam distillation of the residue from the extraction. The 2,4-dinitrophenylhydrazone (2,4-DNP) of III was identical with that prepared from authentic nonanal. The nonsteam-volatile aldehyde mixture (IV and V) was reduced with sodium borohydride.[9] The diol (VI) was removed from the alkaline solution by continuous extraction with ethyl ether. The identity of VI as 1,8-octanediol was established by mixed melting point determinations using the authentic diol and its bisphenylurethane derivative. The remaining fragment (VII) was oxidized by alkaline permanganate,[10] and the product was identified as glutaric acid (VIII) by mixed melting point, gas chromatography, and x-ray diffraction. These cleavage products, with the infrared and near infrared[11] spectra, clearly establish the structure of the C_{22} diene as the previously unknown *cis*-5-*cis*-13-docosadienoic acid.

DISCUSSION

The *cis*-5-*cis*-13-docosadienoic acid found in *Limnanthes* oil appears to be unique. No other dienoic acids with hexylene interrupted unsaturation appear to have been recorded as triglyceride constituents in natural sources. The variance from the common conjugated and methylene interrupted unsaturation[12] has not previously been reported for vegetable oil sources of docosadienoic acid; in fact, only two other docosadienoic acids have been reported: the $\Delta^{13,16}$-isomer from rapeseed oil[12] and the $\Delta^{10,13}$-isomer from ox liver[13] phosphatides. The 5,13-docosadienoic acid did not form a conjugated acid by treatment with alkali. De Surville *et al.* and other workers[14] have shown that even ethylene interrupted unsaturation is difficult to conjugate with alkali. Koyama and Toyama[15a] report that on treatment with alkali 9,12,18- or 9,15,18-eicosatrienoic acid[15b] from the seed oil of *Podocarpus nagi* forms only a conjugated diene instead of conjugated triene. Acids containing ethylene interrupted unsaturation have been reported in fish oils[16–18] and ox liver lipid[19]; however, later work[20] seems to discredit earlier reports.

By analogy with established precedent[21] the tetrahydroxydocosanoic acids, which have not been previously reported, have the di*threo*structure. The 5,6-dihydroxyeicosanoic acids likewise have the *threo*structure. An interesting phenomenon is the occurrence of two C_{22} monoenes with Δ^5- and Δ^{13}- unsaturation together with the 5,13-docosadienoic acid; whereas, petroselinic acid (Δ^6 containing oils are reported to contain oleic and 9,12-octadecadienoic acid[12] rather than the $\Delta^{6,9}$ acid.

EXPERIMENTAL

General methods. Gas chromatographic analyses were carried out with a Burrell Kromo-Tog K-5[22] gas chromatographic instrument. The columns were of U-shaped glass tubing 1.25 to 2.75 meters in length, $^1/_8$ to $^1/_4$ inch inner diameter, and packed with LAC-2R-446 (a polyester of diethylene glycolpentaerythritol and adipic acid) or Apiezon L (a hydrocarbon grease) supported by Johns-Manville Celite 545. The carrier gas was helium and the operating temperature ranged from 185° to 250°, depending on the column liquid phase and the sample. For quantitative determinations of composition, the areas under the peaks were measured by the instrument's automatic integrator. Mixtures of acids were analyzed as their methyl esters. Except where noted, methyl esters were prepared by refluxing the acids 2 hr. under nitrogen in excess 1% sulfuric acid in methanol. Esters were isolated by ether extraction in the usual manner; unchanged acids were removed by washing the ethereal solutions of esters with 5% potassium carbonate. When desired for characterization work, fractionated esters were saponified by refluxing 0.5 hr. with 2*N* ethanolic potassium hydroxide.

Preparation of mixed fatty acids. Coarsely ground seeds of *Limnanthes douglasii* were extracted overnight in a Soxhlet apparatus with petroleum ether (b.p. 33–57°). The bulk of the solvent was evaporated on a steam bath under nitrogen and the remainder was removed *in vacuo* with a rotating evaporator.

A 24.2-g. portion of *Limnanthes* oil was refluxed 30 min. with 150 ml. of 2*N* ethanolic potassium hydroxide. The unsaponifiable material was removed and the free fatty acids (22.9 g.) were obtained in the usual manner.

Low-temperature crystallization. Mixed fatty acids (17.8 g.) were dissolved in 415 ml. of heptane, and the solution was cooled slowly to −55°. After standing 1.5 hr., the mixture was filtered using a filter stick. The solvent was removed yielding 2.7 g. of heptane-soluble acids, iodine

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(7) A. F. McKay, N. Levitin, and R. N. Jones, *J. Am. Chem. Soc.*, **76**, 2383 (1954).

(8) F. D. Gunstone, *J. Chem. Soc.*, **1954**, 1611.

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(15) (a) Y. Koyama and Y. Toyama, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **78**, 1223 (1957). (b) Y. Toyama, Private communication.

(16) Y. Toyama and T. Yamamoto, *Mem. Fac. Eng. Nagoya Univ.*, **3**, 122 (1953).

(17) Y. Toyama and T. Shimo-Oka, *Mem. Fac. Eng. Nagoya Univ.*, **5**, 319 (1953).

(18) T. Aoyagi, *Pharm. Bull. Tokyo*, **5**, 224 (1957).

(19) T. Shimo-Oka and Y. Toyama, *Mem. Fac. Eng. Nagoya Univ.*, **6**, 48 (1954).

(20) Y. Toyama, Y. Iwata, and K. Fujimura, *Fette, Seifen., Anstrichmittel*, **61**, 846 (1959).

(21) F. D. Gunstone, *An Introduction to the Chemistry of Fats and Fatty Acids*, John Wiley and Sons, New York, 1958, pp. 104–109.

(22) Mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

value 143. Gas chromatographic analysis of the methyl esters of the combined heptane-soluble acids indicated 60% C_{22} unknown and 13% C_{20} monoene (Table I).

Fractionation by countercurrent distribution. Methyl esters (7.3 g.) of the heptane-soluble acids were subjected to a 560-transfer countercurrent distribution in a 200-tube automatic Craig-Post apparatus. The solvent system used was mutually saturated acetonitrile and hexane[3] (8:1). The methyl esters were divided evenly among the first four tubes and 40 ml. of acetonitrile (full in the decant position) was placed in each of the remaining tubes. The automatic operation of the instrument introduced 5 ml. of equilibrated hexane to tube O at each transfer stage. As the upper phase progressed past tube 200, it was decanted into an automatic fraction collector, combining two transfers per tube, and was successively collected until 180 fractions had been obtained. The weight distribution plot obtained by evaporating solvent, under reduced pressure, from the contents of selected tubes is shown in Fig. 1. Gas chromatographic analyses of significant fractions are indicated in Table I. On the basis of these analyses, it was not deemed practical to resolve the C_{20} monoene-C_{22} unknown mixture further, and fractions 336 through 394 were combined, yielding 3.7 g. Gas chromatographic analysis of the combined fractions indicated 80.2% of C_{22} unknown, Table I. Free acids were obtained by the usual saponification procedure followed by acidification; these liquid acids gave a neutral equivalent (neut. equiv.) of 327, an iodine value (I.V.) of 141, and a hydrogenation number (H.N.) of 172. Theoretical values for a mixture consisting of 82% C_{22} diene and 17% C_{20} monoene are: neut. equiv., 328; I.V., 136; and H.N., 182.

An 81-mg. portion of the above acid concentrate was hydrogenated in ethanol with a platinum oxide catalyst at room temperature and atmospheric pressure. The suspended catalyst was removed by filtration and after the solvent was removed by evaporation, 76 mg. of white crystals, melting at 72.0–76.5°,[23] was obtained. Recrystallization from 100 ml. of acetone at 0° yielded 50 mg. of crystals, melting at 76.5–78.0°. On recrystallization from ethanol, 32 mg. was obtained, melting point and mixed melting point with authentic docosanoic (behenic) acid (m.p. 78.5–79.0°) was 78–79°.

The infrared spectrum of the concentrate indicated no *trans* unsaturation (little absorption at 10–11 μ), and the near infrared spectrum[11] indicated a *cis*-iodine value of 141 (Wijs iodine values 141).[24] Ultraviolet absorption spectra[4] indicated no conjugated unsaturation before alkali treatment and less than 2% after treatment. Reaction with lipoxidase[5] did not indicate methylene interrupted *cis*-unsaturation.

Hydroxylation[6] of C_{22} diene concentrate. Performic acid was prepared by mixing 0.3 ml. of 30% hydrogen peroxide with 3 ml. of 90% formic acid at room temperature. After 1 hr., the performic acid concentration was 6.0% (determined on a small scale by Wheeler's method[25]).

The C_{22} diene acid concentrate (0.325 g.; 1 mmole) was added at once with stirring and the temperature was maintained between 25 and 30°. After 2 hr., 2 mmoles of performic acid had been used, with no consumption during an additional 0.5 hr. The reaction mixture was diluted with 15 ml. of water and poured over ice; the product was removed by extracting with ether (three times). The combined ether extract was washed with water and dried over sodium sulfate. The viscous liquid (0.383 g.) obtained upon removing the ether was refluxed 1 hr. under nitrogen with 10 ml. of *N* aqueous sodium hydroxide. After diluting the solution with water (50 ml.) and acidifying to Methyl Orange with 2*N* hydrochloric acid, the acids were removed by ether extraction (5 × 100 ml.). The combined ether extract (containing suspended solids) was washed sparingly with cold water and concentrated to *ca.* 125 ml. The mixture was chilled on solid carbon dioxide, and the precipitate was collected on filter paper and dried under reduced pressure, yielding 0.240 g. a white solid (A) melting at 127–132°. The filtrate was evaporated, yielding 0.075 g. of a yellowish solid (B) melting at 71–83°. Fraction A was recrystallized first from 100 ml. of ether and then from 10 ml. of ethyl acetate to yield 0.191 g. of II, melting at 129–131°.

Anal. Calcd. for $C_{22}H_{44}O_6$: C, 65.3; H, 11.0. Found: C, 65.0; H, 10.9.

Fraction B was recrystallized from chloroform:ether (1:1) to yield 0.012 g. melting at 89–112°. The filtrate residue was recrystallized twice from hexane, yielding 0.024 g. melting at 78–81°. This product was presumed to be *threo*-5,6-dihydroxyeicosanoic acid.

Periodate oxidation[8] of the tetrahydroxybehenic acid. A 1.21 g. portion (3 mmoles) of II was suspended in 70 ml. of ethanol and a solution of 1.61 g. of sodium periodate in 75 ml. of *N* sulfuric acid was added. The mixture was heated at 40° for 35 min. with occasional stirring. Suspended solids dissolved slowly leaving only a trace insoluble. The reaction mixture was filtered and collected in 250 ml. of cold water.

Identification of steam-volatile aldehyde. The aqueous solution was extracted (three 100-ml. portions) with pentane-hexane (b.p. 33–57°), and the combined petroleum ether extract was washed with water.

After most of the petroleum ether was removed by distillation (maximum temperature 47°), the residue was steam distilled. The steam volatile aldehyde (III) was treated with 0.60 g. of 2,4-dinitrophenylhydrazine.[26] After dilution with water, the 2,4-dinitrophenylhydrazone was taken up in ether. The crude product (1.00 g.), melting at 84–90°, was chromatographed on paper[27] simultaneously with the 2,4-dinitrophenylhydrazone of authentic nonanal; both had R_f 0.87. By a combination of chromatography on alumina (eluting with benzene) and recrystallizations from ethanol, 0.08 g. melting at 100–103° was obtained from 0.20 g. of crude 2,4-dinitrophenylhydrazone. The mixed melting points with the authentic 2,4-dinitrophenylhydrazone of nonanal (m.p. 103–104°), decanal (m.p. 104–105°), and undecanal (m.p. 104.5–105.5°) were 101–104°, 94–98°, and 85–90°, respectively, thus confirming III to be nonanal.

Sodium borohydride reduction[9] of nonsteam-volatile aldehyde mixture. The remaining aqueous solution of aldehydes (containing IV and V) was extracted with ether, and after removal of most of the ether, the residue was neutralized to indicator paper with 0.2*N* sodium hydroxide, and 150 ml. of 0.25*M* *p*H 9 sodium borate buffer was added. Sodium borohydride (0.091 g. in 110 ml. water) solution was added dropwise over 30 min. with stirring, and after standing overnight, the alkaline solution was diluted with water and extracted continuously with ether. Removal of the ether under reduced pressure yielded a solid (VI, 0.364 g.) melting at 40–54°.

The aqueous alkaline solution was evaporated to dryness under reduced pressure and reserved for characterization of the ω-hydroxy acid (VII).

Characterization of VI. A portion (0.32 g.) of VI was heated 10 min. at 60–65° with 110 ml. of *N* sodium hydroxide. The solution was diluted with water and continuously extracted with ether, yielding 0.22 g. of a semisolid. The product was recrystallized twice from benzene, yielding 0.13 g., melting at 57–58°; mixed melting point with

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(23) Melting points were determined with a Fisher-Johns block and are uncorrected.

(24) Infrared spectrum was measured on undiluted acid in a 0.088-mm. cell with a Baird-Atomic model KM1 recording spectrophotometer. Near infrared spectrum was measured in carbon tetrachloride solution with a Cary model 14 PM spectrophotometer.

(25) D. H. Wheeler, *Oil & Soap*, **9**, 89 (1932).

(26) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley and Sons, New York, 1956, p. 219.

(27) D. F. Meigh, *Nature*, **170**, 579 (1952).

authentic 1,8-octanediol[28] (m.p. 57.5–58.0°) was 57.5–58.0°. A portion of the diol was treated with 0.2 ml. of phenyl isocyanate and with 2 drops of pyridine as a catalyst. The excess reagents were removed under reduced pressure yielding 0.086 g., melting at 169.0–171.5°. The product was recrystallized from ethyl acetate and ethyl acetate–hexane, yielding 0.025 g. with a melting point and a mixed melting point with the authentic bisphenylurethane derivative of 1,8-octanediol (m.p. 172–173°) of 170–172°.

Characterization of the ω-hydroxy acid (VII). A portion of VII (0.40 g.) was dissolved in 20 ml. of water and 0.50 g. of potassium permanganate, and 0.8 ml. of 10% sodium hydroxide was added with stirring. After 30 min. at 20–25° and 2 hr. at 30–35°, the excess permanganate was destroyed by addition of sodium bisulfite, and the reaction mixture was filtered with suction. The filtrate was concentrated, acidified with 2*N* hydrochloric acid, and extracted with ether. The ether extract was evaporated to dryness, and the residue was extracted with hot benzene. After removal of the benzene, the product was recrystallized successively from benzene, chloroform, and chloroform-benzene yielding 0.007 g of VIII, melting at 90–95°; mixed melting point with authentic glutaric acid (m.p. 96.5–97.5°) was 92–96°. The x-ray diffraction pattern of the product was identical to authentic glutaric acid. The methyl esters, prepared with diazomethane,[29] of the combined mother liquor residue consisted of 93% glutaric acid as determined by gas chromatography.

Acknowledgment. The authors thank Mr. C. R. Scholfield and Dr. H. J. Dutton for assistance with the countercurrent distribution; Mr. Henry Zobel for x-ray diffraction analysis of glutaric acid; Mr. E. Selke for infrared spectra; Mrs. Clara McGrew for microanalysis; also Dr. Quentin Jones, Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture, for making available generous quantities of *Limnanthes douglasii* seed.

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(28) Suberic acid was reduced to 1,8-octanediol as outlined by R. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

(29) F. Arndt, *Org. Syntheses*, Coll. Vol. **II**, 165 (1943)

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE UNIVERSITY]

Preparation and Reactions of *sym*-Tetraphenyldisilane

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Received July 25, 1960

The preparation of *sym*-tetraphenyldisilane (I) is discussed. Various reactions of I have been studied in an attempt to correlate the reactions of *sym*-tetraphenyldisilanediol with those of the carbon analog. A series of novel difunctional disilanes was prepared from I and their reactions studied. A useful quantitative method for the estimation of silicon-silicon and silicon-hydrogen bonds is discussed in detail.

The number of known organosilicon compounds containing one or more silicon-silicon bonds is small compared to the number of compounds containing only one silicon atom or isolated silicon atoms. The majority of these disilanes or polysilanes are fully substituted by alkyl or aryl groups. Some *sym*-difunctional disilanes have been encountered as biproducts in the industrial preparation of chlorosilanes.[1]

An accidental encounter with a *sym*-difunctional disilane is reported in connection with the study of steric effects in organosilicon chemistry.[2] It was found that hexachlorodisilane reacted with four moles of *o*-tolyllithium to give *sym*-tetra-*o*-tolyldisilanediol, subsequent to hydrolysis, whereas hexaphenyldisilane could be obtained by the corresponding reaction with phenyllithium.

Attempts to prepare *sym*-dichlorotetraphenyldisilane by the action of four moles of phenylmagnesium bromide on hexachlorodisilane failed as did the attempted introduction of six phenyl groups by the use of the Grignard reagent.[3]

It was discovered that chlorodiphenylsilane is coupled by the action of magnesium to form *sym*-tetraphenyldisilane.[4] This reaction is comparable

$$2(C_6H_5)_2SiHCl + Mg \longrightarrow (C_6H_5)_2SiHSiH(C_6H_5)_2 + MgCl_2$$

to the coupling reaction of chlorotriphenylsilane with magnesium.[5] This type of coupling may involve the highly reactive silyl Grignard reagent which was likewise considered to be an intermediate in the reaction of cyclohexylmagnesium bromide with chlorotriphenylsilane.[6]

The preparation of *sym*-tetraphenyldisilane is very sensitive to the effectiveness of the initiation. This may be performed by the addition of ethyl iodide in much the same way as difficult preparations of Grignard reagents are initiated. Table I

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