FISHERIES RESEARCH BOARD OF CANADA
Translation Series No. 899

Studies on antarctic whale oils by gas-liquid chromatography using a hydrogen flame ionization detector. VII. Identification of 4,8,12-trimethyltridecanoic acid as a constituent of whale oil

By Yoshihiko Sano

Original title: Gasukuromatogurafi niyoru nanpyoyosan geiyu no kenkyu (dai-7-ho) geiyukoseishibosan 4,8,12 trimetirutridecan san no dotei.

From: Yukagaku (Journal of Oil Chemists' Society), Vol. 16, pp. 56-61. 1967.

Translated by the Translation Bureau (NT)
Foreign Languages Division
Department of the Secretary of State of Canada

Fisheries Research Board of Canada
Technological Research Laboratory,
Halifax, N. S.

1967

DEPARTMENT OF THE SECRETARY OF STATE
BUREAU FOR TRANSLATIONS

FOREIGN LANGUAGES DIVISION

CANADA

SECRÉTARIAT D'ÉTAT
BUREAU DES TRADUCTIONS

DIVISION DES LANGUES ÉTRANGÈRES

TRANSLATED FROM – TRADUCTION DE	INTO – À
Japanese	English

SUBJECT – SUJET

Oil Chemistry (Fishery Science)

AUTHOR – AUTEUR

SANO, Yoshihiko

TITLE IN ENGLISH – TITRE ANGLAIS

Studies on ~~the~~ Antarctic whale oils by gas-liquid chromatography using a hydrogen flame ionization detecter. VII. Identification of 4,8,12-trimethyltridecanoic acid as a constituent of whale oil

TITLE IN FOREIGN LANGUAGE – TITRE EN LANGUE ÉTRANGÈRE

Gasukuromatogurafi niyoru Nanpyoyosan gaiyu no kenkyu(dai-7-ho)
Geiyukoseishibosan 4,8,12 trimetirutridecan san no dotei

REFERENCE – RÉFÉRENCE (NAME OF BOOK OR PUBLICATION – NOM DU LIVRE OU PUBLICATION)

Yukagaku(Journal of Oil Chemists' Society), Vl. 16, p56 -61,1967

PUBLISHER – ÉDITEUR

CITY – VILLE	DATE	PAGES
	1967	p56 -61

REQUEST RECEIVED FROM
REQUIS PAR Fisheries Research Board

OUR NUMBER
NOTRE DOSSIER N° 8806

DEPARTMENT
MINISTÈRE

TRANSLATOR
TRADUCTEUR nt

YOUR NUMBER
VOTRE DOSSIER N° 769-18-14

DATE COMPLETED
REMPLIE LE May 31'67

DATE RECEIVED
REÇU LE April 25,1967

Yukagaku, V.16, p56--61,1967.

Studies on the Antarctic Whale Oils by Gas-Liquid Chromatography Using a Hydrogen Flame Ionization Detector. VII. Identification of 4,8,12-trimethyltridecanoic Acid as a Constituent of Whale Oil

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A minor component "C" (ECL value, 14.3_5[1] 2)) in the multi-branched-chain fatty acids, separated earlier from whale oil, was identified by gas-liquid chromatography as 4,8, 12-trimethyltridecanoic acid, which was synthesized for comparison from both farnesol and phytol and confirmed by means of infrared absorption, nuclear magnetic resonance, and mass spectrometry.

The content of this acid in the fin whale blubber oil investigated was approximately 0.005% of the total weight of the acids.

The acid was also present as a constituent of the oils from sperm whale blubber as well as blubber whale bone and sei whale blubber, as previously reported[3].

1. Introduction

Of three components in the multibranched-chain fatty acids, separated earlier from whale oils, two had been previously identified as 3,7,11,15-tetramethylhexadecanoic acid (ECL value, 17.5[1) 2)]) and 2,6, 10,14-tetramethylpentadecanoic acid[4] (ECL value, 16.2[1)2)]). The structual examination on the third component "C"(ECL value, 14.3_5[1)2)]) will be reported in the present paper.

First of all, methyl-3,7,11-trimethyldecanoate and methyl-4,8,12-trimethyldecanoate were synthesized from both farnesol and phytol and were confirmed by means of infrared absorption, nuclear magnetic resonance and mass spectrometry. A comparison was made between these synthesized substances and the component "C" by gas-

liquid chromatography (GLC). As a result, the presence of 4,8,12-trimethyltridecanoic acid has been corroborated as a constituent of the oils from fin whale blubber as well as blue whale bone and sei whale blubber and sperm whale blubber.

2. Experimental and Results

The oil sample and the procedure used were similar to those reported previously.[3)4)] However, experimental conditions are shown in figures to ensure clear picture.

2.1 Synthesis of Methyl-3,7,11-trimethyldecanoate

Methyl-3,7,11-trimethyldecanoate was synthesized through the pathway as described in Fig-1.

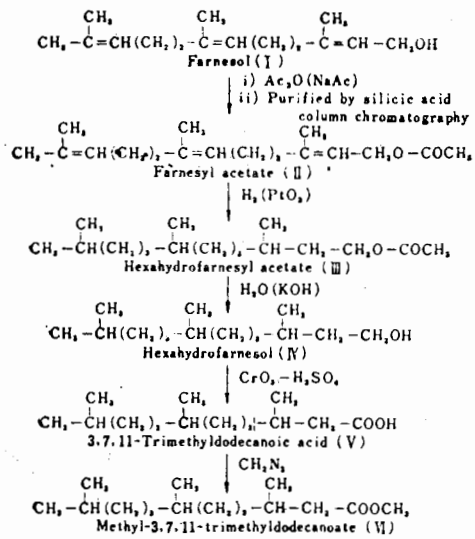


Fig.-1 Synthetic pathway of methyl-3, 7, 11-trimethyldodecanoate from farnesol.

2.1.1 Acetylation of Crude Farnesol and Purification of Acetate

In order to remove impurities, acetylation of crude farnesol was first performed and then fractionation through chromatography on the silicic acid column.

Farnesol (Takasago Flavour Industry Co.), 2.05 g, was treated

with 20 ml glacial acetic acid in the presence of 200 mg sodium acetate for 2.5 hr at 90°C. It yielded 2.33 g of acetylide which was then developed on a column (inner diameter, 20 mm; length,90 mm) packed with 15.0 g silicic acid with n-hexane to remove hydrocarbons and coloured impurities. Thus, 1.61 g of colourless, purified farnesyl acetate was obtained. A single spot was shown on its thin-layer chromatogram and no OH absorption was observed near 3,400 cm^{-1} on its infrared absorption spectrum, while a strong one appeared in the vicinity of 1,230 cm^{-1} which was caused by C-O-expansion-contraction-vibration.

2.1.2 Hydrogenation and GLC Analysis of Farnesyl Acetate

In 20 ml of n-hexane was dissolved 1.00 g of purified farnesyl acetate which was then subjected to hydrogenation for 8 hours p9 at approx. 30°C with 200 mg of platinum black catalyst. After the removal of the catalyst by passing it through a layer of silicic acid, 995 mg of colourless hydride was obtained. GLC analysis performed under the conditions usually employed for methyl ester analysis[4] detected the main component that comprised 86 % besides two minor components.

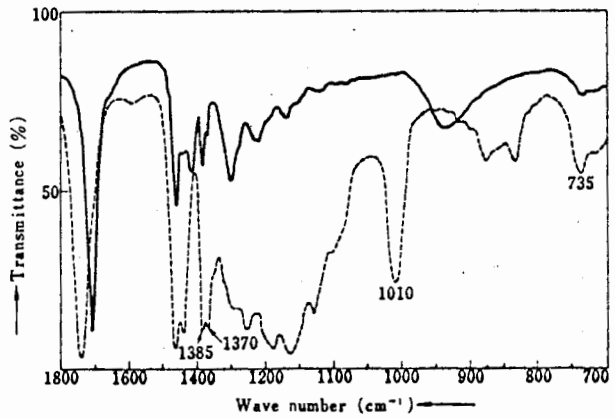
2.1.3 Hexahydrofarnesol (III)

Two hours treatment of 905 mg of hydride described above with 10 ml of 1N-alcoholic potash at approximately 60°C and extraction of the reacted product with n-hexane produced 744 mg of the extract. An infrared absorption typical of the primary alcohol was observed on its infrared absorption spectrum. Furthermore, isoprenoid structure was recognized on the basis of the doublet near 1,380 cm^{-1} and another absorption near 735 cm^{-1} [6]. This alcohol

was subjected to purification using a column (inner diameter, 20mm; length, 50 mm) packed with 10.0 g of silicic acid, as the result of which 64 mg of colurless liquid was obtained from the elute on development with 50 ml n-hexane. The main constituent of this purified alcohol was found to be hydrocarbons through TLC. Since practically no hydrocarbon was detected in the second n-hexane eluted fraction (59 mg), further elution was performed with 50 ml n-hexane containing 20% ether. The elute, 551 mg, was thus collected which showed a single spot on TLC analysis.

2.1.4 Methyl-3,7,11-trimethyldecanoate (do)

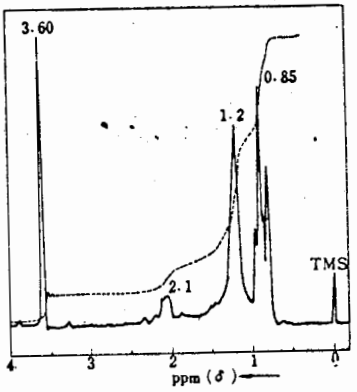
The above purified alcohol, 610 mg, was dissolved in 21 ml acetone, to which 3.0 ml of chromic acid mixed solution[4] was slowly added while stirring with a magnetic stirer at approx. 30°C and then was subjected to treatment for one hour. After letting stand overnight at room temperature, the reacted liquid was filtered. The filtrate was extracted with n-hexane on addition of salt water, and 611 mg of the colourless oily matter was collected. As shown in Figure-2, the absorption of fatty acids were indicated on the infrared absorption spectra. (Fig-2)



All IR analyses were made on thin films of the sample by using a model IR-S spectrophotometer (Japan Spectroscopic Co., Ltd.).

Fig.-2 Infrared absorption spectra of 3, 7, 11-trimethyldodecanoic acid and its methyl ester (dotted line).

The results of GLC analysis of methyl ester converted from the above acid with diazomethane showed 96% purity. Its infrared absorption spectrum is shown in Figure-2, which indicated doublet absorption caused by the isopropyl group near 1,380 cm^{-1},[6] and there was another absorption of three methylne chains-$(CH_2)_3$- . On the basis of the above two absorptions, isoprenoid structure was identified.[5] In addition, it was learned from the absorption near 1,010 cm^{-1} that the first methyl branched-chain from the carbomethoxy group existed at the third (β position) carbon atom.[7] In order to confirm the number of branches, neclear magnetic resonance absorption spectra was determined using Varian-A-60 NMR spectrometer (Fig-3).



Varian A-60 high resolution NMR spectrometer equipped with a Varian NMR integrator.
Solvent : CCl_4
Filter bandwidth : 1 cps,
R.F. Field : 0.4 mG
Sweep time : 500 sec
Sweep width : 500 cps
Spectrum amp : 2.0×10

Fig.-3 Nuclear magnetic resonance spectrum of methyl-3, 7, 11-trimethyldodecanoate.

The signal at 3,60 ppm (δ) was caused by the carbomethoxy group.[6] [8] Using its area strength as the standard (corresponding to three protons), the signal of the methyl group at 0.85ppm(δ) had the area strength of 12 protons.[6] Therefore, it was learned

that the number of methyl branches of this methyl ester was three. Also present near 1.2 ppm(δ) was a signal equivalent to 15 protons caused both by the methylene group and the methyne group. Another signal corresponding to two protons was found in the vicinity of 2.1 ppm(δ) caused by the carbomethoxy group and the methylene group at the α-position.[6)8)] Thus all the results of above analyses support the identification of the substance as methyl-3,7,11-trimethyldecanoate. p10

2.2 Synthesis of Methyl-4,8,12-trimethyltridecanoate

Synthesis of methyl-4,8,12-trimethyltridecanoate was carried out by Arndt-Eistert method[9)] from 3,7,11-trimethyldecanoic acid which had been synthesized from farnesol, and also from phytol after converting it to phytone with potassium permagnate through Barbier-Wieland reaction method[10)] and through the synthetic pathways shown in Fig-4. (Fig-4)

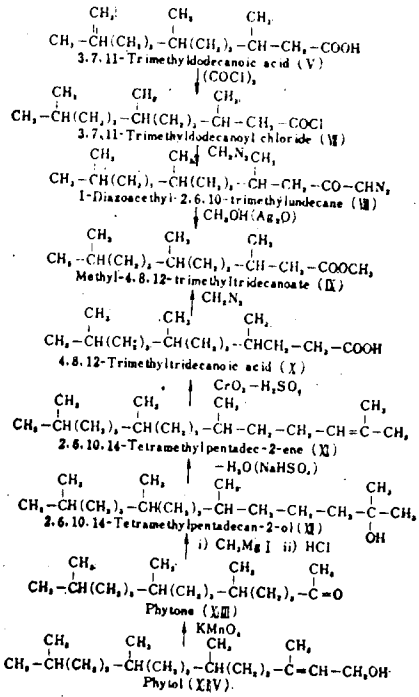


Fig.-4 Synthetic pathway of methyl-4, 8, 12-trimethyltridecanoate from both 3, 7, 11-trimethyldodecanoic acid and phytol.

2.2.1 3,7,11-trimethyldodecanoyl chloride (VII)

3,7,11-trimethyldedecanoic acid (V), 81 mg , was poured in 50 ml capacity pear shaped flask. Added to it was 0.5 ml of distilled oxalic chloride and, after attachment of calcium chloride tube, was left stand overnight at room temperature. The reacted product was then treated for 30 minutes at approx. 45°C under reduced pressure with tap aspirator. After cooling in ice water and on addition of 10 ml n-hexane, it was moved to separating funnel filled with ice cubes. Light yellowish liquid, 84 mg, was obtained after washing twice in ice water and drying over sodium sulfate (anhydride) and on removal of the solvent under reduced pressure. On its infrared spectrum, a strong absorption band of $\nu_{C=O}$ caused by -I effect of chlorine /was found/ in the region near 1,800cm^{-1}, while practically no absorption band of untreated fatty acids was detected.

2.2.2 1-diazoacetyl-2,6,10-trimethylundecane (VIII)

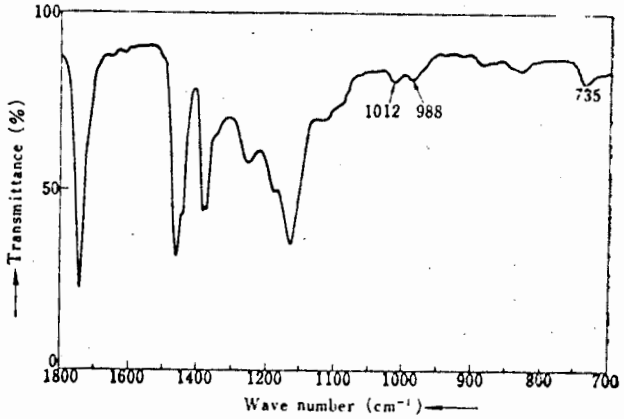
Approx. 15ml of the ether solution of diazomethane[12] prepared from approx. 0.5 g of nitrosomethyl urea[12] was dried completely in draft over granular potassium hydroxide. Added slowly dropwise to it was approx. 3 ml of absolute ether solution of 62 mg (VII) to allow reaction at approx. 10°C. After letting the reacted liquid stand overnight at room temperature and on removal of the insolubles through a silicic acid thin layer and of ether, 50 mg of yellowish oily matter was produced. Infrared spectra indicated a sharp absorption band in the region near 2,100 cm^{-1} caused by the diazo group[13] and another strong absorption band of $\nu_{C=O}$[13] was observed in the vicinity of 1,630cm^{-1}

which had been shifted downfield because of the resonance structure

$$R-C(=O^{(+)})-CH^{(-)}-N\equiv N$$

2.2.3 Formation of Methyl-4,8,12-trimethyltridecanoate(IX) by Rearrangement of Diazoketone (VIII)

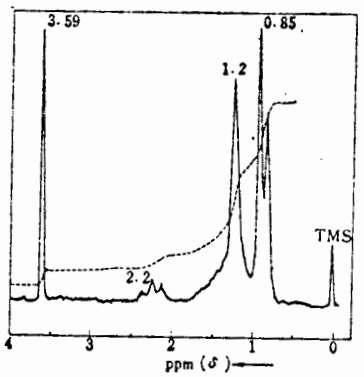
Diazoketone(VIII), 32 mg, was poured in 50 ml capacity pear shaped flask and added to it was 6 ml of absolute methanol and 30mg silver oxide (reagent, special grade), which was then stirred by a magnetic stirir for four hours at approx. 65°C. After cooling and removal of the insolubles and on addition of salt water, n-hexane extraction gave 25 mg of the extract, which was then purrified through a silicic acid column, thus, 17 mg of colourless liquid was obtained. TLC analysis indicated a single spot in the region usually assigned to multibranched-chain saturated fatty acid methyl esters. Its infrared spectra also demonstrated absorption band typical of multibranched-chain fatty acid methyl esters. From the doublet absorption near 1,000 cm^{-1}(1,012 cm^{-1}, 988 cm^{-1} 7), it was learned that methyl branched-chain existed at the fourth carbon atom (γ position) (fig-5).



The analysis was made on thin films between rock-salt disks by using a twin-beam spectro-photometer model IR-S (Japan Spectroscopic Co., Ltd.).

Fig.-5 Infrared absorption spectrum of methyl-4, 8, 12-trimethyltridecanoate.

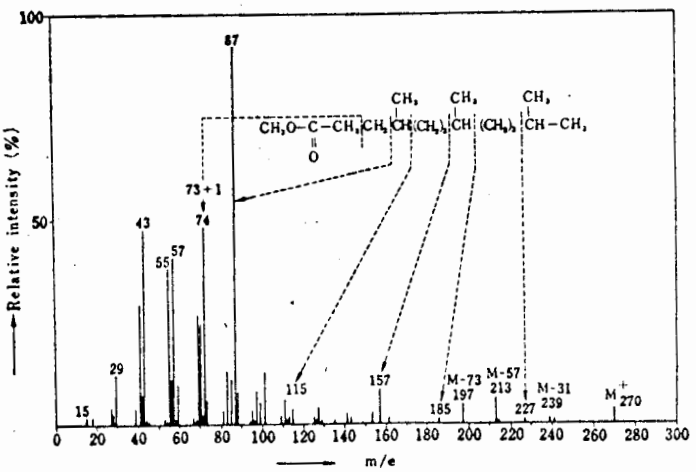
That the main component made up 85% and that methyl-3,7,11-trimethyldodecanoate was present to the extent of 8% was learned from GLC analysis. As shown in Figure-6, nuclear magnetic resonance absorption spectra were similar to those shown in Fig-3. However, some differeing features of the nmr spectra from those in Figure-3 may be described as follows: The signal of the methylene group and the methyne group in the vicinity of 1.2 ppm(δ) was equal to approx. 17 protons with an increase of two protons. Another signal of the methyl group near 0.85 ppm(δ) was less complicated than that in Fig-3, whereas the signal (equivalent to 2 protons) of the methylene group at α position of the carbomethoxy group was somewhat more complex and showed a downfield shift of approx. 0.1 ppm(δ). Although the difference in the conditions under which the measurements were taken might be a factor for this, it may be more appropriately attributed to the difference in chemical shifts since practically no shift was observed in the signal caused by the carbomethoxy group. (Fig-6)



Solvent : CCl_4, Filter bandwidth : 0.4 cps, R.F. Field : 0.35 mG, Sweep time : 500 sec, Sweep width : 500 cps, Spectrum amp : 4.0×10.

Fig.-6 Nuclear magnetic resonance spectrum of methyl-4, 8, 12-trimethyltridecanoate.

Furthermore, measurement of the mass spectra confirmed that this main component was the desired methyl-4,8,12-trimethyltridecanoate. In other words, as shown in Figure-7, its molecular formula is $C_{17}H_{34}O_2$ from the presence of its molecular ion at m/e 270 and from that of methylester (M-31, m/e239). Its base peak was at m/e 87 and from a considerably strong peak present at m/e 115 the methyl branched-chain /was/ learned to be at the fourth (ζ position) carbon atom, which agreed with the results of the infrared absorption spectroscopy. In addition, since relatively strong peaks were detected at m/e 87, 115, 157, 185 and 227, respectively, it was learned to have isoprenoid structure, and, moreover, the methyl branched-chains were found to exsit at 4,8, and 12 carbon atoms, respectively. All these results of instrumental analyses agreed with those reported by Sen Gupta et al.[7] Thus, it was corroborated that the synthesis of the desired methyl-4,8,12-trimethyldecanoate can be achieved through the synthetic pathway as described in Figure-4. (Fig-7)



Hitachi RMU-6 D Massspectrometer.
Max. *m/e* : 600, Vac. : 2.0×10^{-7}mmHg, Chamber volt : 70 V, Sample pres. : 5.5×10^{-7}mm Hg, Total emission : 80 uA, E.M. sens. : 100, Ion chamber temp : 250°C, H.V. volt : 1.2 kV, Evap. temp. : 130°C.

Fig.-7 Mass spectrum of methyl-4, 8, 12-trimethyltridecanoate.

2.2.4 Synthesis of 4,8,12-trimethyltridecanoic Acid from Phytol

To 1.42 g of phytol(XIV), (Tokyo Kasei K.K., Special Grade Reagent), 300 ml of the saturated acetone solution with potassium permagnate was added and then left stand for three days at room temperature. The precipitate was separated by filtration and 706 mg of oily matter was obtained through n-hexane extraction after addition of salt water to the filtrate.. After purification on the silicic column and through TLC analysis, a single spot with Rf 0.47 was detected. Its infrared spectra indicated a strong absorption of $\gamma_{C=O}$ of keton in the vicinity of 1,720 cm^{-1} and GLC analysis showed 99% purity.

Grignared reaction of 464 mg of phytone using ether solution of methyl magnesium iodide prepared from the thin sheet of magnesium, 50 mg, and 290 mg of methyl iodide gave 424 mg of the product. The alcohol fraction was fractionated through TLC for preparation and the infrared spectra determination indicated an absorption typical of the tertiary alcohol near 1,150 cm^{-1}. Added to 64 mg of this alcohol (XII) was 10 mg of sodium sulfate(anhydrous, acidic) for dehydration by heating for five minutes at 200°C under the reduced pressure of 65 mmHg. It was then subjected to purification on the column packed with 1.0 g of silicic acid, which yielded 50 mg of the colourless product. After confirming it as unsaturated multibranched-chain hydrocarbons from the results of TLC analyses and the infrared spectra, and on treatment with the mixed liquid of chromic acid[4] in a manner almost similar to that previsously stated,[4] 42 mg of n-hexane extract was collected.

It was further chromatogramed by TLC and the multibranched-chain fatty acid fraction was obtained after the infrared absorption spectroscopy, and following methylesterification with diazomethane and purification on the silicic acid column, 18 mg of colourless methylester was obtained. By means of infrared absorption spectroscopy and GLC analysis, identification of the main component as methyl-4,8,12-trimethyldecanoate was corroborated.

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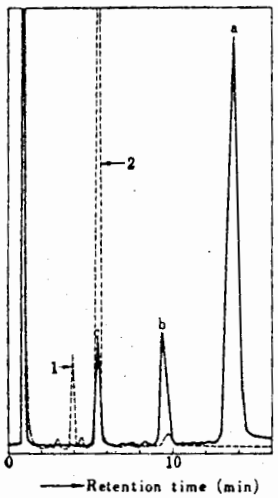
2.3 Identification of Component "C" of Multibranched-Chain Fatty Acid

Comparison of the above mentioned synthesized standard substances, i.e. methyl-3,7,11-trimethyldodecanoate and methyl-4,8,12-trimethyltridecanoate with the component "c" as a multi-branched-chain trace consituent of whale oil by GLC confirmed that the retention time of methyl-4,8,12-trimethyldecanoate was in complete agreement with that of the component "C". Figure-8 shows one example of this. (Fig-8)



Shimadzu model GC-IC gas chromatograph
Column……3 mm i.d. × 185 cm, 10% PEGA on Diabase B, 80-100 mesh, 210°C.
Detector……Shimadzu hydrogen flame ionization detector model FID-IB, H_2 : 25 ml/min, Air : 0.8 kg/cm², Sens. : 10^2, Range : 1.6V.
Carrier gas He : 1.4 kg/cm²,
Chart speed : 5 mm/min.

Fig.-8 Gas-liquid chromatograms of the component "C" in the multibranched-chain fatty acid methyl ester fraction from blue whale bone oil, methyl-3, 7, 11-trimethyldodecanoate (1) and methyl-4, 8, 12-trimethyltridecanoate (2).

These standard substances and the multibranched-chain fatty acid methyl ester fraction were then reduced to alcohol by lithium aluminum hydride in a similar manner to that previously reported[2] and then was converted to acetate through acetylation with glacial acetic acid.and It was then subjected to comparison by GLC under the same analytic conditions as used for analysis of the fatty acid methyl ester. The retention time agreet in the case of acetate also; the component "c" was thus identified as 4,8,12-trimethyltridecanoic acid. This acid was also found present as a consituent of the oils from sperm whale as well as sei whale and fin whale blubber besides blue whale bone oil as reported earlier.[2]

3. Discussion

There have already been several reports published on the synthesis of methyl-4,8,12-trimethyltridecanoate. Among them, Mayers et al (1963)[15] first oxidized α-tocopherol in glacial acetic acid with chromic acid and then through methylesterification obtained the desired methyl-4,8,12-trimethyltridecanoate(purity, 73.5%). They also produced the ester with 84.5% purity from ozonising phytol and after oxidation of the resultant phytone with sodium hypobromate and on esterification, converting it to C_{16} acid through Barbier-Wieland reaction(using phenylmagnesium bromide for Grignard reaction, and p-toluenesulfonic acid for dehydration, and chromic acid for oxidation in glacial acetic acid), and finally by methylesterification with methanol in the presence of concentrated sulfuric acid. On the other hand, Sen Gupta et al (1966)[7] synthesized the substance through the pathway described below using farnesol as starting material: Farnesol $\xrightarrow{H_2(\text{Raney-Nickel})-}$ Hexahydrofarnesol $\xrightarrow{P/I_2}$

Hexahydrofanesyl iodide $\xrightarrow{KCN}$ Hexahydrofarnesyl nitril $\xrightarrow{NaOH}$ 4,8,12-trimethyltridecanoic acid $\xrightarrow{CH_3OH/H^+}$ methyl-4,8,12-trimethyltridecanoate. The author attempted to synthesize the substance using farnesol and phytol as starting materials through different method and pathway and in the unit of mg. For purification, either silicic acid chromatography or TLC was employed other than distillation. Since all the synthetic intermediates were oily matters, purity was determined through TLC or GLC analyses. And the structure of methyl-4,8,12-trimethyltridecanoate was confirmed by means of TLC analysis, infrared absorption, nuclear magnetic resonance, and mass spectrometry.

The author has previously reported on the existence of 4,8,12-trimethyltridecanoic acid in whale oil at the convention of Japan Fishery Sciences Society in April this year (1966).[16] More recently, Sen Gupta et al (1966)[7] reported the presence of the same substance in fish oil (species unknown) to the extent of approx. 0.15%. The blubber oil of fin whale which was used as the oil sample in the present experiments may exist to the extent of approx. 0.005%.

To date, among the multibranched-chain fatty acids occurring in natural fat and oil as the constituents, structures of three substances, namely, 3,7,11,15-tetramethylhexadecanoic acid,[3)7)17)22)] 2,6,10,14-tetramethylpentadecanoic acid,[4)7)23)24)] and 4,8,12-trimethyltridecanoic acid[7] were confirmed. It is expected more and more acids will be studied and confirmed. Iverson et al (1965)[25] reported the presence of numerous multibranched-chain fatty acids (the number of branches, 3 --5) with unknown structure in butterfat

or lard. Kaufman et al (1966)[26] also reported the presence of C_{19}--C_{28} fatty acids with 4 branches in butterfat and veal fat. However, practically no datum to support the presence of these substances was indicated.

Thus, it is likely that many a multibranched /-chain/ fatty acid is present, though in extremely small amount, in animal fat. Those existing in relatively larger amount in whal oil are the above-mentioned three, however, as a result of continued close examinations, some other components with multibranched-chains may be detected, and the extent of their presence will be unlikely to exceed the range of 1 % of the weight of total the fatty acid. It is the wish of the author to compare and study quantitatively the distribution of multibranched-chain fatty acids according to species, age and part of body of whales. Physiological significance and biosynthetic pathways of these multibranched-chain fatty acids are not yet known.

In closing, the author wishes to extend his sincere appreciation to Mr. T. Yamada of Tohoku University for his assistance in carrying out the determinations of nuclear magnetic resonance absorption spectra and mass spectra and to Mr. Y. Yamaguchi of Takasago Flavour Co., for supplying farnesol. His deep gratitude also goes to Dr. Y. Ishikawa, director of the research laboratory, Miyoshi Oil and Fat Co., for his permission to publish the research.

(Received on Oct. 17,1966)

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