

Studies Related to Pristane

V. The Constitution of Zamene

PER KOCH CHRISTENSEN and NILS ANDREAS SÖRENSEN

Institutt for Organisk Kjemi, Norges Tekniske Högskole, Trondheim, Norway

The saturated hydrocarbon, pristane, was discovered in 1917 by Tsujimoto¹ in the liver oil of the basking shark. He found that fractional distillation gave a crude pristane which had an iodine number of 4.4, whilst refining with sulphuric acid gave the hydrocarbon free from unsaturated material.

In 1923, Toyama² investigated the pristane content of six Japanese elasmobranch fish oils. He found that the pristane fractions, which had been purified by distillation only, still had considerable iodine numbers.

Fish	Iodine number
<i>Cetorhinus maximus</i> Gunner	2.7
<i>Scymnorhinus licha</i> Bonaterre	9.8-11.3
<i>Centrophorus spec.</i>	15.9
<i>Zameus squamulosus</i>	} (mixed oil)
<i>Centroscymnus owstonii</i>	
<i>Chlamydoselachus anguineus</i> Garman	{ 22.2
	{ 81.6

In 1935, Tsujimoto³ showed that this unsaturation was due to an olefine hitherto unknown. He isolated this new hydrocarbon, which he named "zamene", by addition of bromine followed by removal of the unchanged pristane by vacuum distillation. Zamene was regenerated from its dibromide with zinc and shown to have the composition $(\text{CH}_2)_n$ and the following constants:

$$d_4^{20} = 0.7948$$

$$n_D^{20} = 1.4470$$

$$\text{I. N.} = 66.2$$

Catalytic hydrogenation gave a saturated hydrocarbon which Tsujimoto considered to be identical with pristane. He held the opinion that both pristane and zamene were C_{18} -hydrocarbons. In the previous four communications of this series⁴⁻⁷ it was shown that pristane is the C_{19} -hydrocarbon, 2,6,10,14-tetramethyl-pentadecane or *nor*-phytane. As mentioned in the third communication the *nor*-phytane structure of pristane was supported by a preliminary investigation of zamene. Zamene was oxidised with peracids and the oxide hydrolysed to the corresponding α -glycol which was separated from Pristane by means of partition and distillation. Splitting of the α -glycol with lead tetra-acetate gave formaldehyde and a liquid ketone whose physical constants resembled those of 2,6,10-trimethylpentadecan-14-one, the classical degradation product of phytol⁸⁻¹⁰. We were, however, unable to isolate crystalline derivatives of this important degradation product and, therefore, were led to a detailed reinvestigation of this degradation of zamene.

In this reinvestigation we met with unexpected difficulties. The starting material was, as in our preliminary investigation, the foreruns of basking shark liver oil. Fractional distillation gave a crude pristane fraction which was contaminated with zamene and the fatty alcohols, cetyl, stearyl and oleyl alcohols. The bulk of these fatty alcohols was removed by several crystallisations at -15° although some oleyl alcohol remained in the crude pristane. To remove the final traces of alcohol sodium was pressed in, the jelly of alcoholates filtered off and the filtrate distilled over sodium. This procedure is the same as that used by Tsujimoto¹ and by us in our preliminary investigation. The more intensive this pretreatment the worse was the purity of the product on oxidation with peracid and hydrolysis to α -glycol. On distillation of the expected α -glycol at 10^{-4} mm, the products distilled over a range of at least 70° , the lowest boiling fraction analysed for one oxygen per C_{19} , the middle fraction, which boiled between $120-130^{\circ}$ at 10^{-4} mm gave analytical figures which corresponded approximately to $C_{19}H_{40}O_2$ but on lead tetraacetate titration¹¹ gave α -glycol values of only 20-30 %. Preparative oxidation of the middle fraction with lead tetra-acetate gave carbonyl compounds of differing boiling points.

As any pronounced inhomogeneity of the zamene fraction was highly improbable some rearrangement must have taken place in the reactions we have mentioned. The more prolonged each treatment the more these side reactions would tend to predominate. Lüttringhaus, Sääf, Sucker and Borth have shown in a paper¹² published in 1945 that the double bond of a mono-olefine may be displaced as a result of distillation over metallic sodium. As soon as we heard of this paper (which owing to war conditions was only reprinted in 1949) we repeated our experiments with the exclusion of the treatment with metallic

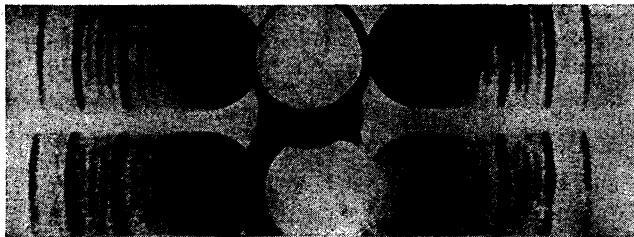


Fig. 1. Debye-Scherrer diagrams of the semicarbazone of 2,6,10-trimethyl-pentadecan-14-one. I from Phytol II from Zamene.

sodium. To remove the remaining fatty alcohols, the crude pristane was treated with excess 3,5-dinitro-benzoyl chloride and pyridine in the cold and then for 3 hours at 80°. The mixture of pristane, zamene and dinitro-benzoates was separated by chromatography on alumina. As will be seen from the experimental section, pristane is eluted more readily than zamene but the difference in adsorptivity on ordinary activated alumina is insufficient for a preparative separation on a small scale. The pristane-zamene mixture was oxidised with OsO_4 according to Criegee¹³.

The osmic ester was decomposed with mannitol-potassium hydroxide and the α -glycol obtained from zamene purified by partition and distilled at 10^{-4} mm. On this occasion, we obtained only a small forerun ($< 10\%$), the rest distilling at 118—122° (air bath temperature) practically without residue. This α -glycol was a viscous oil, $n_D^{20} = 1.4582$, $d_4^{20} = 0.887$, $M_D \text{ obs.} = 92.49$, $M_D \text{ calc.} = 92.99$, and analysing for $\text{C}_{19}\text{H}_{40}\text{O}_2$. As will be seen from the experimental section the analytical figures tend to preclude a difference of $\pm \text{CH}_2$.

The elementary formula $\text{C}_{19}\text{H}_{40}\text{O}_2$ was confirmed fully by lead tetra-acetate oxidation which gave formaldehyde — characterised as its dimedone derivative — and 2,6,10-trimethyl-pentadecan-14-one characterised as its semicarbazone, m. p. 64°. The semicarbazone of the same ketone, prepared by ozonolysis of phytol, melted at 65.5° (older statements in the literature gave m. p.'s 64.5—67°⁸⁻¹⁰), mixed m. p. 65°. For purposes of further identification, Debye-Scherrer diagrams of the two semicarbazones were taken and, as may be seen from Fig. 1, were identical.

EXPERIMENTAL

The starting material was foreruns from industrial distillation of basking shark liver oil most kindly placed at our disposal by Chem. Eng. Alf Brautaset, Jahres Kjemiske Fabrikker A/S, Sandefjord. About 63.5% of the crude oil boiled between 105—115°

on fractionation at 0.2–0.5 mm using a 70 cm column. This fraction was left for some days at -17°C and the solid fatty alcohols removed by filtration at that temperature (loss about 8 %). The crude pristane fraction had an iodine number (Wijs) of 4.0 and analysed as follows:

C	84.94	H	14.53	100-(C + H)	0.53
»	84.61	»	14.72	100-(C + H)	0.67

150 g of this crude oil was shaken in a closed vessel for 43 hours at room temperature with 15 ml anhydrous pyridine and 6 g 3,5-dinitrobenzoyl chloride. The mixture was then heated for 3 hours at 80°C , shaken 3 times with 5 % NaHCO_3 solution, then with water, and the pristane ester mixture dried over anhydrous MgSO_4 . On chromatography on activated alumina and elution with petroleum ether, the first half of the eluate contained 122 g, of oil, $n_D^{20} = 1.4386$ and the remainder contained 17 g of oil $n_D^{20} = 1.4391$. Both these fractions were rechromatographed on activated alumina in petroleum ether. The first fraction was separated into 7 equal parts and the second into 3. The iodine numbers were as follows:

Fraction	1a	1b	1c	1d	1e	1f	1g
I. N.	0.34	0.92	1.12	1.13	1.20	1.18	1.23
Fraction	2a	2b	2c				
I. N.	0.54	2.58	11.9				

The iodine numbers clearly demonstrate that chromatographic separation of zamene and pristane would be practicable with oils somewhat enriched in zamene.

82 g of this chromatographically purified pristane-zamene mixture with iodine number 1.04 was treated with 1 g osmium tetroxide in 50 ml anhydrous ether. After 2 days 1 ml of pyridine was added and the dark precipitate separated from the solution. Both the precipitate and filtrate were decomposed in methylene chloride with 1 % potassium hydroxide containing 10 % mannitol. The precipitate gave only a small quantity of pure pristane (C + H = 100.1). The filtrate was partitioned three times between petroleum ether and 92 % methanol. The hypophasic part was distilled at 10^{-4} mm. Forerun, below 90° , 13 mg. Fraction boiling $118-122^{\circ}$, 119 mg $n_D^{20} = 1.4582$, $d_D^{20} = 0.887$. No residue.

Calc. for $\text{C}_{18}\text{H}_{38}\text{O}_2$ (286.5)	C = 75.46,	H = 13.37 %
$\text{C}_{19}\text{H}_{40}\text{O}_2$ (300.5)	C = 75.93,	H = 13.42 %
$\text{C}_{20}\text{H}_{42}\text{O}_2$ (314.5)	C = 76.37,	H = 13.46 %

Found	C = 75.87,	H = 13.09 %
	C = 75.86,	H = 13.21 %
	C = 76.17,	H = 13.50 %
Mean	C = 75.97,	H = 13.27 %

42 mg of the glycol, $C_{19}H_{40}O_2$ was treated with 10 ml *N*/10 lead tetra-acetate in acetic acid¹⁴. The formaldehyde was expelled by means of a stream of nitrogen at 40–50° for 4 hours and absorbed in a solution of dimedone in water. On standing, crystals of the dimedone derivative appeared, m. p. 190° (corr.). Mixed m. p. with a synthetic sample showed no depression. Debye-Scherrer diagrams of the two dimedone derivatives proved their identity.

The oxidation solution was diluted with water, extracted with ether and the ethereal extracts washed until neutral, dried and distilled at 0.001 mm, air bath temperature: 75°. As may be observed from the table the physical constants of the distillate are in good agreement with those reported in the literature for 2,6,10-trimethyl-pentadecan-14-one.

Table 1. Physical constants of 2,6,10-trimethyl-pentadecan-14-one. (All data recalculated to 20° C.)

Author	n_D^{20}	d_4^{20}	R_D^{20} (calc. = 85.33)
Willstätter <i>et al.</i> from phytol ⁸	1.44434	0.844	84.50
» » » » » ⁹	1.44516	0.834	85.65
Fischer » » » » ¹⁰	1.4450	0.8355 ₅	85.49
» » » synthetic ¹⁰	1.4453	0.8349 ₅	85.61
Fischer and Löwenberg » ¹⁵	1.4452	0.8369 ₅	85.44
Heilbronn <i>et al.</i> » ¹⁶	1.44315	0.83965	84.73
This paper from zamene	1.4450	0.8392	85.09

The distillate gave a crystalline semicarbazone with semicarbazide hydrochloride which on recrystallisation from methanol gave colourless needles m. p. 64°. The semicarbazone of 2,6,10-trimethylpentadecan-14-one, obtained by ozonolysis of phytol, melted at 65.5°, mixed m. p. 65°. Debye-Scherrer diagrams *cf.* Fig. 1.

SUMMARY

The constitution of the olefine hydrocarbon, zamene, found in some elasmobranch fish oils, as 2,6,10,14-tetramethyl pentadec-1-ene was established by degradation to 2,6,10-trimethyl-pentadecan-14-one and formaldehyde.

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