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Studies Related to Pristane

III. The Identity of *Nor*phytane and Pristane

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In the two first communications in this series [1, 2] we have shown that the saturated hydrocarbon pristane, earlier considered a octadecane, is at least a nonadecane. As the eight possible mono-methyl-octadecanes all showed m. p. between — 16.5° and + 13° C whereas pristane does not solidify at — 80°, we concluded that pristane belongs to the more branched alkanes. The only branched alkanes that are found in living nature are the hydrogenated terpenes; therefore we have continued the comparison of pristane with saturated compounds related to known diterpenes.

Owing to its easy accessibility, we first [1] synthesized the previously known hydrocarbon crocetane = 2,6,11,15-tetramethyl-hexadecane. The physical constants of this compound we found to be in agreement with the data of Fischer and Löwenberg [3] who synthesized this hydrocarbon the first time. As will be seen crocetane comes rather close to the values given for pristane, but the crocetane values

	d_4^{20}	n_D^{20}
Crocetane		
(mean of Fischer, and our own data)	0.7880	1.4404
Pristane	0.7827–0.7843	1.4385–1.4398

fall a little higher. Terpenes with symmetrically transposed isoprene units such as in crocetane are only known in squalene and the carotenoids. The diterpenes of certainly known constitutional formula have either regularly connected isoprene units or the end unit distorted through a Wagner-rearrangement. [4] The regularly constructed diterpene alkane is phytane = 2,6,10,14-tetramethyl-hexadecane. Willstätter, Mayer and Hüni [5] produced phytane as early as 1911; unfortunately the only physical constant given was

$d_4^0 = 0.803$. We, therefore, had to prepare phytane once more and the synthesis followed the line:

Phytol → Dihydrophytol → Dihydrophytylbromide → Phytane

(for details see experimental part). Phytane thoroughly purified showed the following constants:

	d_4^{20}	n_D^{20}
Phytane:	0.7907	1.44225

The difference in density and refractive index between crocetane and phytane is in agreement with the difference expected from the regularities worked out by Calingaert [6] and Francis [7].

The two most probable terpenoid-alkanes thus definitely differ from pristane. The physical constants of this saturated diterpene strengthen the results of the molecular weight determinations of Berner [1], giving the molecular formula to $C_{19}H_{40}$. For comparison we therefore prepared *nor*phytane = 2,6,10,14-tetramethyl-pentadecane. According to Fischer and Löwenberg [8] phytol was degradated to 6,10,14-trimethyl-pentadecanone-2. CH_3MgI when added to this ketone gave 2,6,10,14-tetramethyl-pentadecanol-2. This carbinol was converted to the corresponding ethylene compound which was in turn hydrogenated to *nor*phytane = 2,6,10,14-tetramethyl-pentadecane, whose physical constants were as follows:

	d_4^{20}	n_D^{20}
*Nor*phytane	0.7833	1.4386
Pristane	0.7827—0.7843	1.4385—1.4398

The comparison with pristane shows the most excellent agreement. On the basis of the before mentioned regularities [6, 7] of the physical constants of the alkanes, it can be foreseen that no other nonadecane of reasonable structure will have density and refractive index as low as *nor*phytane; these regularities thus heavily augment the possibility that pristane is identical with *nor*phytane.

Of course, we have tried to demonstrate this identity through mixed melting point determinations, but these failed, as we did not succeed in crystallizing these hydrocarbons at all. Below — 85° C pristane and *nor*phytane as well as phytane and crocetane successively become thicker, between — 99 and — 100° C they all congeal. And this congelation appears at the same tem-

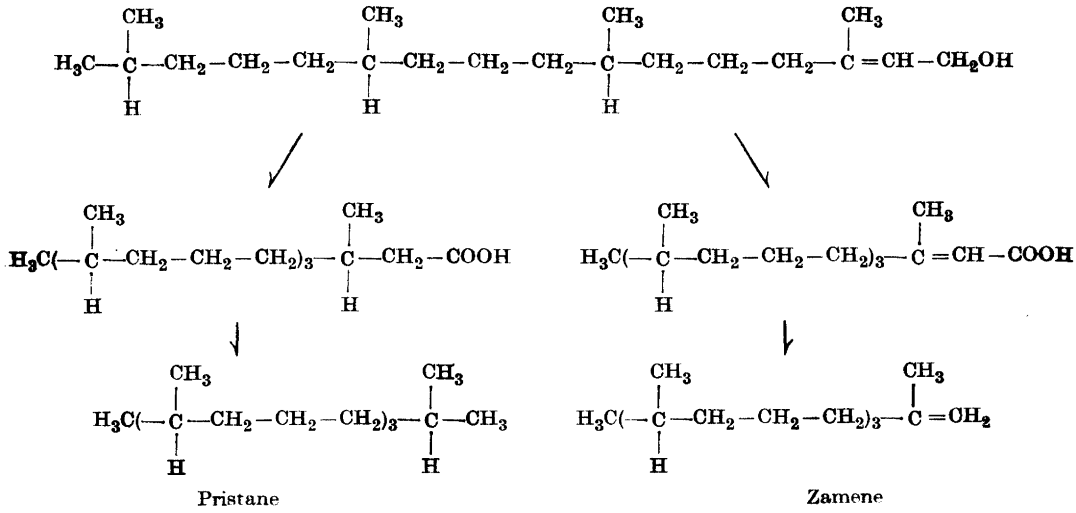
peratures with mixtures of pristane and *nor*phytane as with mixtures of pristane and for example phytane. Certainly the identical congelation circumstances of pristane and the said terpenoid alkanes significantly point to the correctness of our working hypothesis that pristane itself is of a terpenoid nature.

As mentioned in a lecture given by one of us [9] at the 6th Scandinavian chemical meeting in Lund the 28th August 1947, we have succeeded in degrading pristane to oxygen containing terpenoid compounds of lower molecular weight partially through chlorination with tert-butylchloride-$AlBr_3$ according to Bartlett, Condon and Schneider [10], splitting off HCl with alcoholic potassium hydroxide followed by ozonization, and partially through nitration with 100 % HNO_3 according to Grundmann [11] and ozonization of the alkali-soluble fraction of the nitro-compounds. Both methods, however, gave very complex mixture of compounds, and we have met great difficulties in the preparation of definite degradation products.

A confirmation of the identity of pristane and *nor*phytane was however achieved from quite another side. As is known, Tsujimoto [12] in 1935 demonstrated that the pristane fraction of Basking Shark liver oil contains quite small amounts of an ethylene hydrocarbon, called zamene, which on hydrogenation gave an alkane with constants identical with pristane. In cooperation with Chem. Eng. Per Koch Christensen we have tried to elucidate the structure of zamene. The details of this work will follow in another publication of this series. It may be mentioned, however, that zamene was transformed by peracids into its epoxide, the epoxide hydrolyzed to the corresponding α-glycol. This glycol which was separated from pristane through 'Entmischung' between petrol and 90 % methanol analyzed for $C_{19}H_{40}O_2 \pm CH_2$.

When this α-glycol was split up with lead tetraacetate according to Criegee, it gave two components; formaldehyde, and a liquid monooxygen-compound with physical constants and elementary composition very close to the ketone $C_{18}H_{36}O$ from phytol, *viz.* 6,10,14-trimethyl-pentadecanone-2. Hence the ethylene hydrocarbon zamene ought to have the constitution 2,6,10,14-tetramethyl-pentadecene-1.

The constitutional formulae deduced for pristane and zamene at once suggests a process for this unusual occurence of C_{19}-terpenes in nature. Both hydrocarbons bear close relations to the fundamental aliphatic diterpene phytol. Dehydrogenation of the primary alcohol group to carboxyl, accompanied or not by hydrogenation of the α,β-ethylene bond, gives rise to phytane- or to phytene-carboxylic acid respectively. On decarboxylation these acids generate the two hydrocarbons pristane and zamene.



It is impossible for the time being to predict at what stage these transformations of phytol take place in nature, the authors being inclined to guess at enzymatic processes of the bacterial flora of the intestine of either the zooplankton or the intermediate food animals, but the constitution of these hydrocarbons ought to exclude synthetic processes in the elasmobranch fishes themselves.

EXPERIMENTAL

Phytane

Phytol ('L. Light & Co. Ltd') was carefully fractionated at 0.001 mm, and the main fraction was hydrogenated at ordinary temperatures with PtO_2-catalyst. In accordance with the statements of Willstätter, the fractionation gave a small forerun of phytane, the main fraction boiling at 100° bath temperature at 0.001 mm was dihydrophytol, $n_D^{20} = 1.4541$, $d_4^{20} = 0.8431$. These constants are in agreement with older data: Willstätter [5] $d_4^{20} = 0.8398$, $n_D^{20} = 1.45213$, Kuhn and Suginomé [13] $n_D^{20} = 1.4538$.

Dihydrophytol was transformed into its bromide with anhydrous HBr-gas according to *Organic Synthesis* XV p. 35 a 24. Dihydrophytylbromide b. p. 105°, 0.001 mm $n_D^{20} = 1.4641$, $d_4^{20} = 0.9675$, $M_D = 103.1$, $M_{D,\,calc.} = 102.3$.

$C_{20}H_{41}Br(361.4)$	Calc.	C 66.45	H 11.43	Br 22.12
	Found	» 66.66	» 11.50	» 22.34

Kuhn and Suginomé [13] have emphasized the difficulties in getting Grignard-reactions of dihydrophytylbromide. Only with small amounts of completely dry, freshly destilled ether did the reaction start. When the reaction had ceased, dry NH_4Cl and then water

were added. Phytane b. p. 75° bath temperature 0.001 mm. The main fraction was purified with 100 % H_2SO_4, redestilled once over Na and then slowly fractionated at 0.001 mm, main fraction 69°—71° bath temperature. $d_4^{20} = 0.7907$ calc. by A.W. Francis $d_4^{20} = 0.7895$, the value given by Willstätter, $d_4^0 = 0.803$, corresponds exactly to $d_4^{20} = 0.7895$, using the mean temperature coefficient dD/dt = 0.000676 of $C_{18}-C_{21}$ alkanes given in Egloff: *Physical constants of hydrocarbons.* Vol. I (1939).

Table 1. Dispersion of phytane.

$$R_{\lambda,\,\text{calc.}} = \frac{92.381 \cdot \lambda^2}{\lambda^2 - 0.7883 \cdot 10^6} \qquad \text{o} : \lambda_0 = 887.8 \text{ ÅU}$$

λ	n_λ^{20}	$R_{\lambda,\,\text{obs.}}$	$R_{\lambda,\,\text{calc.}}$
6678.1	1.43961	94.03	94.04
5895.9	1.44225	94.52	94.52
5875.7	1.44234	94.54	94.54
5015.6	1.44688	95.38	95.37
4921.9	1.44752	95.50	95.49
4713.1	1.44911	95.79	95.78
4471.5	1.45113	96.17	96.17

2,6,10,14-Tetramethyl-pentadecanol-2

Phytol was freshly fractionated at 0.001 mm and treated with ozone in glacial acetic acid. The phytol-ozonide was decomposed with zink dust and water. Acidic reaction products were withdrawn from the ethereal solution of the ketone through repeated washings with sodium carbonate, and 2,6,10-trimethyl-pentadecanone fractionated cautiously at 0.0001 mm (b. p. bath temperature 76—80° C). The physical constants given in literature and found by us are as follows:

	n_D^{20}	d_4^{20}
Willstätter	1.4443	0.844
Fischer from phytol	1.4452	0.8357
» synthetic	1.4455	0.8351
Fischer & Löwenberg synthetic	1.4454	0.8371
Found this publ.	1.4445	0.8370

4.25 g 2,6,10-trimethyl-pentadecanone was slowly reacted at ordinary temperature with the calculated amount CH_3MgI and worked up in the usual way. 2,6,10,14-tetramethyl-pentadecanol-2 is an oil, b. p. 100° at 0.001 mm.

$C_{19}H_{40}O$ (284.4)	Calc.	C 80.21	H 14.17
	Found	» 79.71	» 14.14
	»	» 80.32	» 14.14

$d_4^{20} = 0.8367$.

Table 2. Dispersion of 2,6,10,14-tetramethyl-pentadecanol-2.

$$R_{\lambda,\,\text{calc.}} = \frac{89.131 \cdot \lambda^2}{\lambda^2 - 0.7832 \cdot 10^6} \qquad \text{o} : \lambda_0 = 885 \text{ ÅU}$$

λ	n_λ^{20}	$R_{\lambda,\,\text{obs.}}$	$R_{\lambda,\,\text{calc.}}$
6678.1	1.44653	90.71	90.72
5895.9	1.44927	91.19	91.19
5875.7	1.44938	91.21	91.20
5460.7	1.45118	91.53	91.53
5015.6	1.45394	92.01	92.00
4471.5	1.45823	92.76	92.76
4358.3	1.45935	92.96	92.96

Norphytane = 2,6,10,14-tetramethyl-pentadecane

By dehydration of 2,6,10,14-tetramethyl-pentadecanol-2 2 isomeric *nor*phytenes may arise, *viz.* one with *iso*propylidene (Δ2.3) and one with methylene-grouping (Δ1.2). We have made no efforts to determine the composition of the ethylenemixture formed by heating 2,6,10,14-tetramethyl-pentadecanol-2 with $KHSO_4-K_2SO_4$ at 150° C for 4 hours, as both of them will generate the same alkane on hydrogenation. The resulting liquid norphytene showed the following constants $n_D^{20} = 1.4482$, $d_4^{20} = 0.79899$, $M_{D,\,\text{obs.}} = 89.29$, $M_{D,\,\text{calc.}} = 89.47$.

*Nor*phytene was hydrogenated by bubbling hydrogen through the ethylene at 90° C in the presence of a $Pt-SiO_2$-catalyst (17 % Pt). *Nor*phytane was purified in the usual way with sulfuric acid and fractionation over Na. B. p. 0.001 mm 68° bath temperature. $d_4^{20} = 0.7833$.

Table 3. Dispersion of Norphytane = 2,6,10,14-tetramethylpentadecane.

$$R_{\lambda,\,\text{calc.}} = \frac{87.988 \cdot \lambda^2}{\lambda^2 - 0.7886 \cdot 10^6} \qquad \text{o} : \lambda_0 = 888 \text{ ÅU}$$

λ	n_λ^{20}	$R_{\lambda,\,\text{obs.}}$	$R_{\lambda,\,\text{calc.}}$
6678.1	1.43596	89.56	89.57
5895.9	1.43863	90.03	90.03
5875.7	1.43872	90.05	90.05
5460.7	1.44054	90.38	90.38
5015.6	1.44320	90.85	90.84
4921.9	1.44382	90.96	90.95
4713.1	1.44535	91.23	91.23
4471.5	1.44735	91.59	91.60
4358.3	1.44849	91.79	91.80

SUMMARY

For comparison with pristane, phytane was resynthesized, and *nor*-phytane = 2,6,10,14-tetramethyl-pentadecane synthesized the first time.

*Nor*phytane	$d_4^{20} = 0.7833$	$n_D^{20} = 1.4386$	Congelation point = — 100° C.
Our purest pristane	$d_4^{20} = 0.78267$	$n_D^{20} = 1.43848$	Congelation point = — 100° C.

As the regularities worked out by the petroleum chemists predict that no other nonadecane of reasonable structure will show density and refractive index as low as *nor*phytane, it is concluded that *nor*phytane and pristane are identical = 2,6,10,14-tetramethyl-pentadecane.

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