

Studies Related to Pristane

II. The Methyl-Octadecanes

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In the first communication in this series¹ it was shown that the saturated hydrocarbon pristane found in different fish liver oils is — in contrast to previous statements in literature — at least a nona-decane. As there were very few comparison substances in the nona-decane-series we decided to synthesize all the eight hitherto unknown mono methyl-octadecanes. All these syntheses, which will be found in the experimental part, are of a routine character, the only difficulty being to procure starting materials of great purity, the value of the entire work resting on the purity of the hydrocarbons obtained.

As the purity of a saturated hydrocarbon is difficult to ascertain by elementary analysis, we preferred to refine the final hydrocarbons with 100 % H₂SO₄ followed by redistillation over metallic sodium to constant physical properties (n_D^{20} and d_4^{20}), taking care that the refractive and dispersion constants were in accordance with the standard values of a saturated hydrocarbon. The dispersion was calculated by a method worked out by one of us². We have been satisfied when $\lambda_{\text{calc.}}$ differs by less than 5 ÅU from the standard value for saturated hydrocarbons, viz. 885.2 ÅU.

Table 1. Physical constants of the *x*-methyl-octadecanols-*x*.

<i>x</i>	M. p.	d_4^{20}	n_D^{20}	R_D , obs. (R_D , calc. = 91.463)	$R_{\lambda = \infty}$ obs. ($R_{\lambda = \infty}$ calc. = 89.386)	λ_0 ÅU
3	+ 32—32.5°	—	—	—	—	—
4	+ 16°	0.8394	1.45192	91.36	89.32	880.1
5	+ 6.5—7.0°	0.83745	1.45080	91.38	89.335	881.3
6	— 23°	0.8385	1.45103	91.305	89.26	882.1
9	— 23°	0.8355	1.45085	91.60	89.54	883.5

All but one of the methyl-octadecanes — the 2-methyl-octadecane, which was synthesized according to Wurz — were prepared via the tertiary alcohols. Five of these tertiary alcohols were saturated, their constants are given in Table 1.

The two remaining carbinols were both prepared from Δ^{10} -undecenoic acid, and were used for the further synthesis as methyl-octadecene-17 ols. They were both liquids, m. p. below -80° , their constants are given in Table 2.

Table 2. Physical constants of the *x*-methyl-octadecene-17-ols-*x*.

<i>x</i>	d_4^{20}	n_D^{20}	R_D , obs. (R_D , calc. = 90.996)
7	0.8470	1.4561	90.62
8	0.84296	1.4565	91.12

By splitting off water from the tertiary carbinols, three different ethylenes may arise; all, however, giving the same saturated hydrocarbon. Because of this uncertainty we have not designated any particular position to the ethylene bond. Table 3 gives the ethylenes from the carbinols in Table 1; Table 4 the dienes from the unsaturated alcohols in Table 2.

Table 3. Physical constants of the *x*-methyl-octadecenes.

<i>x</i>	d_4^{20}	n_D^{20}	R_D , obs. (R_D , calc. = 89.471)
3	0.8011	1.4490	89.16
4	0.7973	1.44975	89.72
5	0.7964	1.4489	89.67
6	0.7962	1.4494	89.78
9	0.7978	1.4487	89.48

Table 4. Physical constants of the *x*-methyl-octadeca-dienes (17,-).

<i>x</i>	d_4^{20}	n_D^{20}	R_D , obs. (R_D , calc. = 89.00)
7	0.8081	1.4553	88.79
8	0.8048	1.4557	89.21

Finally, Table 5 gives the eight theoretical mono-methyl-octadecanes. As these saturated hydrocarbons could be much more thoroughly purified than the intermediate compounds, the agreement between the constants of these 8 compounds is much better than between the different isomeric alcohols and olefines. The 2-methyl-octadecane, prepared by Wurz-synthesis, shows the greatest deviations, and although its m. p. + 12.5—13.2° fits in very well between the values + 5° for 2-methyl-heptadecane³ and + 18.3° for 2-methylnonadecane⁴, we are convinced that our preparation of 2-methyl-octadecane is not perfectly pure. The low values shown by the constants of the 2-methyl-compounds are, however, in accordance with the regularities which the petroleum chemists have worked out, chiefly on the basis of the physical constants of the lower parafines⁵.

Table 5. Physical constants of the eight mono-methyl-octadecanes.

x	M. p.	d_4^{20}	n_D^{20}	R_D , obs. (R_D , calc. = 89,938)	$R_{\lambda = \infty}$, obs. ($R_{\lambda = \infty}$, calc. = 87,877)	λ_0 ÅU
2	+ 12.5—13.2°	0.77935	1.43707	90.212	88.146	892
3	+ 0.5°	0.7871	1.44110	90.039	88.005	885.4
4	— 1.0°	0.78607	1.44081	90.105	88.075	883.6
5	— 14— — 13°	0.78595	1.44067	90.094	88.071	884.25
6	— 4.0°	0.78589	1.44065	90.0975	88.067	884.25
7	— 16.5— — 16°	0.7871	1.44125	90.065	88.006	889.56
8	— 10°	0.78595	1.44098	90.149	88.109	887.07
9	— 16.5°	0.78555	1.44055	90.119	88.087	884.1

The general formula given by Calingaert *et. al.*⁵ gives the following values for 2-, 3- and 4-methyl-octadecane:

	d_4^{20} calc. according to Calingaert ⁵
2-Methyl-	0.78317
3- » -	0.78770
4- » -	0.78689

Our 2-methyl-compound shows far too great a depression, most likely due to lack of homogeneity in our preparation. The agreement is fairly good in the 3 and 4 series. Calingaert *et. al.* have given no formula for a more central location of the methyl group. As will be seen from Table 5, the physical constants remain remarkably uniform from 4-methyl onwards to 9-methyl.

As to the problem of the constitution of pristane, it will be seen that of the physical constants of pure pristane (*cf.* Sørensen and Mehlum¹),

$$d_4^{20} = 0.7827-0.7843; n_D^{20} = 1.4385-1.4398, R_D = 90.08-90.12,$$

the density and refractive indices of pristane are intermediate between the values for 2-methyl-octadecane and the remaining seven methyl-octadecanes. The molecular refraction is in complete accordance with the values found for the eight methyl octadecanes. As will be seen, however, all the methyl-octadecanes *have m. p. between -16.5 and +13°, whereas pristane does not solidify at -80°*. We conclude that whether its molecular formula is $C_{19}H_{40}$ or $C_{20}H_{42}$, pristane will have to be more branched than a monomethyl-derivative. So, to some extent, the physical constants of the synthesized mono-methyl-octadecanes increase the possibility that pristane is terpenoid in structure.

EXPERIMENTAL

2-Methyl-octadecane

From pure cetyl alcohol from spermaceti, m. p. 48—49°, cetyl iodide was prepared by the method given in *Org. Syntheses* 15 p. 29. From iso-propyl iodide and cetyl iodide the 2-methyl-octadecane was prepared by the standard Wurz-procedure.

Table 6. Dispersion of 2-methyl-octadecane.

$$d_4^{20} = 0.7793_5; \lambda_0 = 892 \text{ \AA}U, R_{\lambda=\infty} = 88.146.$$

λ	n_{λ}^{20}	$R_{\lambda, \text{obs.}}$	$R_{\lambda, \text{calc.}}$
6678.1	1.43447	89.744	89.748
5895.9	1.43707	90.212	90.214
5875.7	1.43717	90.230	90.226
5790.7	1.43761	90.309	90.289
5460.7	1.43897	90.553	90.563
5015.6	1.44173	91.048	91.027
4921.9	1.44240	91.168	91.141
4713.1	1.44396	91.447	91.422
4471.48	1.44597	91.806	91.801
4358.3	1.44704	91.997	92.001

3-Methyl-octadecane

Pure palmitic acid was converted into palmitoyl chloride with SOCl_2 (cf. Hann and Jamieson⁶). After distillation the chloride was poured under vigorous stirring into excess diluted ammonia. The palmitoyl amide was dried and crystallized from alcohol, m. p. 104—105°. Palmitoyl amide was converted into palmitonitrile with SOCl_2 according to Oldham and Ubbelohde⁷. Further, the palmitonitrile was transformed into methyl *n*-pentadecyl ketone with CH_3MgI according to the same authors; m. p. of this ketone 48—49°.

3-Methyl-octadecanol-3

To 2.4 g methyl *n*-pentadecyl ketone in abs. ether was slowly added the theoretical amount of C_2H_5MgBr in ether, the reaction mixture was left at room temperature for 15 hours and worked up in the usual way. B. p. in air bath 103—105°/0.001 mm.

$C_{19}H_{40}O$ (284.4)	Calc.	C 80.21	H 14.17
	Found	79.9	14.4

From 3-methyl-octadecanol-3 water was split off with $KHSO_4 \cdot K_2SO_4$, 1 hour at 150°. B. p. for this ethylene 87° in air bath/0.001 mm. It was redistilled over Na. The observed density agrees well with Eijkman's⁸ $d_4^{20} = 0.8044$.

The ethylene was hydrogenated to 3-methyl-octadecane with PtO_2 (Adams) without solvent at 90—100° for 2 hours and refined as described above, b. p. 85—87° in air bath at 0.001 mm.

Table 7. Dispersion of 3-methyl-octadecane.

$$d_4^{20} = 0.7871, \lambda_0 = 885.4 \text{ \AA}U, R_{\lambda = \infty} = 88.005.$$

λ	n_{λ}^{20}	R_{λ} obs.	R_{λ} calc.
6678.1	1.43849	89.575	89.579
5895.8	1.44110	90.039	90.035
5875.7	1.44119	90.055	90.050
5460.7	1.44300	90.376	90.381
5015.6	1.44571	90.855	90.836
4471.48	1.44989	91.593	91.596
4358.3	1.45096	91.781	91.793

4-Methyl-octadecane

From pure myristic acid *n*-tetradecanol-1 or myristyl alcohol was prepared as in *Org. Syntheses* 10 p. 62. The alcohol was converted into myristyl bromide by a procedure analogous to that given in *Org. Syntheses* 1 p. 7 for laurylbromide. 11.2 g myristyl bromide and 0.98 g Mg in abs. ether was heated until it had dissolved and slowly reacted at 10° with 3.2 g methyl *n*-propyl ketone (prepared according to Meerwein⁹), the carbinol 4-methyl-octadecanol-4, was worked up in the usual way.

$C_{19}H_{40}O$ (284.4)	Calc.	C 80.21	H 14.17
	Found	79.94	14.55

Table 8. Dispersion of 4-methyl-octadecanol-4.

$$d_4^{20} = 0.8394, \lambda_0 = 880.11 \text{ \AA}U, R_{\lambda = \infty} = 89.324.$$

λ	n_{λ}^{20}	R_{λ} obs.	R_{λ} calc.
6678.1	1.44926	90.897	90.903
5895.8	1.45192	91.362	91.360
5875.7	1.45201	91.378	91.374
5460.7	1.45387	91.703	91.706
5015.6	1.45662	92.183	92.162
4471.48	1.46083	92.915	92.924
4358.3	1.46195	93.110	93.121

4-Methyl-octadecane was prepared from the carbinol in the same way as the 3-methyl-compound.

Table 9. Dispersion of 4-methyl-octadecane.

$$d_4^{20} = 0.78607; \lambda_0 = 883.6 \text{ \AA}; R_{\lambda=\infty} = 88.078.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} calc.
6678.1	1.43819	89.639	89.647
5895.8	1.44081	90.105	90.102
5875.7	1.44090	90.121	90.116
5460.7	1.44271	90.443	90.446
5015.6	1.44539	90.918	90.899
4471.48	1.44953	91.649	91.657
4358.3	1.45062 ₅	91.842 ₅	91.853

5-Methyl-octadecane

By the same procedure as that used in the synthesis of methyl *n*-pentadecyl ketone from palmitic acid, pure myristic acid was transformed into methyl *n*-tridecyl ketone m. p. 39°. This ketone in abs. ether (temperature below 10° C) was added slowly to the theoretical amount of $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{-Mg-Br}$, and 5-methyl-octadecanol-5 was worked up as usual.

$\text{C}_{19}\text{H}_{40}\text{O}$ (284.4) Calc.	C 80.21	H 14.17
Found	80.21	14.21

Table 10. Dispersion of 5-methyl-octadecanol-5.

$$d_4^{20} = 0.83745, \lambda_0 = 881.31 \text{ \AA}, R_{\lambda=\infty} = 89.335.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} calc.
6678.1	1.44816	90.915	90.918
5895.8	1.45080	91.379	91.377
5875.7	1.45090	91.397	91.391
5460.7	1.45273	91.717	91.724
5015.6	1.45550	92.202	92.181
4471.48	1.45974	92.942	92.946
4358.3	1.46082	93.130	93.147

5-methyl-octadecane was prepared from the carbinol in the usual way.

Table 11. Dispersion of 5-methyl-octadecane.

$$d_4^{20} = 0.78595, \quad \lambda_0 = 884.25 \text{ \AA}, \quad R_{\lambda = \infty} = 88.071.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} , calc.
6678.1	1.43802	89.623	89.639
5895.8	1.44067	90.094	90.092
5875.7	1.44076	90.110	90.107
5460.7	1.44256	90.430	90.436
5015.6	1.44525	90.906 ₅	90.889
4471.48	1.44940	91.640	91.645
4358.3	1.45048	91.831	91.842

6 - M e t h y l - o c t a d e c a n e

Lauryl alcohol and lauryl bromide were prepared from pure lauric acid by the methods given in *Org. Syntheses* and used above for myristic acid. Ethyl *n*-butylacetoacetate was prepared as in *Org. Syntheses* 7 p. 36, and decomposed to methyl *n*-amyl ketone according to Meerwein⁹. 18 g lauryl bromide in a few ml ether was Grignardized with 1.7 g magnesium. The methyl *n*-amyl ketone dissolved in ether was, as usual, added slowly at a temperature below 10°.

6-methyl octadecanol-6 was worked up in the usual way.

$C_{19}H_{40}O$ (284.4) Calc.	C 80.21	H 14.17
Found	80.30, 80.02	14.50, 14.23

Table 12. Dispersion of 6-methyl-octadecanol-6.

$$d_4^{20} = 0.83385, \quad \lambda_0 = 882.15 \text{ \AA}, \quad R_{\lambda = \infty} = 89.261.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} , calc.
6678.1	1.44838	90.840	90.846
5895.8	1.45103	91.305	91.305
5875.7	1.45118	91.331	91.319
5460.7	1.45297	91.644	91.653
5015.6	1.45582	92.142	92.110
4471.48	1.46000	92.871	92.876
4358.3	1.46105	93.053	93.074

The 6-methyl-octadecane was prepared in the usual way from the tertiary carbinol.

Table 13. Dispersion of 6-methyl-octadecane.

$$d_4^{20} = 0.78589, \lambda_0 = 884.25 \text{ \AA}, R_{\lambda = \infty} = 88.067.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} , calc.
6678.1	1.43805	89.635	89.639
5895.8	1.44065	90.097 ₅	90.093 ₅
5875.7	1.44074	90.113	90.108
5460.7	1.44253	90.431	90.438
5015.6	1.44527	90.917	90.892
4471.48	1.44939	91.646	91.651
4358.3	1.45045	91.833	91.848

7-Methyl-octadecane

Methyl *n*-hexyl ketone was synthesized according to Newman and Booth jr.¹⁰ by slowly adding an ethereal solution of $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Mg-Br}$ to a mixture of acetic anhydride and abs. ether at -75 — -80° , and stirring at this temperature for two hours. B. p. methyl *n*-hexylketone 172° .

From castor oil Δ^{10} -*n*-undecenoic acid was prepared according to Jones and Pyman¹¹. The recrystallized acid was transformed into the ethyl ester by means of abs. $\text{C}_2\text{H}_5\text{OH} + \text{HCl}$ at 70°C .

B. p. 134 — $138^\circ/13$ mm. $n_D^{20} = 1.4377$, $d_4^{20} = 0.8768$

M_D , obs. = 63.49 M_D , calc. = 63.42. After the abovementioned Bouveault-Blanc reduction the Δ^{10} -undecenoic acid ethyl ester was transformed into Δ^{10} undecenol-1. B. p. $133^\circ/16$ mm, $n_D^{20} = 1.4509$.

The 1-bromundecene-10 was prepared from Δ^{10} undecenol-1 by the procedure given by Karrer and Helfenstein¹² for the preparation of farnesylbromide from farnesol. 1-Bromundecene-10 distilled at 63° in air bath at 0.001 mm.

$$n_D^{20} = 1.4692, d_4^{20} = 1.083 \quad M_D, \text{ obs.} = 59.96, \quad M_D, \text{ calc.} = 60.29$$

15 g 1-bromundecene-10 in 15 ml abs. ether was Grignardized with 1.55 g Mg, and methyl *n*-hexyl ketone in ether added slowly at below $+10^\circ$. 7-Methyl-octadecene-17-ol-7 was isolated by fractional distillation at 0.001, as — through some side reaction — it was originally contaminated by some hydrocarbon with high boiling point.

$\text{C}_{19}\text{H}_{38}\text{O}$ (282.4)	Calc.	C 80.73	H 13.57
	Found	» 81.00	» 13.76

7-Methyl-octadecene-17-ol-7 was transformed into 7-methyl-octadecane in the usual way.

Table 14. Dispersion of 7-methyl-octadecane.

$$d_4^{20} = 0.7871, \quad \lambda_0 = 889.5 \text{ \AA}, \quad R_{\lambda=\infty} = 88.006.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} calc.
6678.1	1.43859	89.593	89.595
5895.8	1.44125	90.065	90.056
5875.7	1.44135	90.083	90.070
5460.7	1.44317	90.405 ₅	90.405
5015.6	1.44587	90.883	90.864
4471.48	1.45002	91.616	91.633
4358.3	1.45116	91.816 ₅	91.831

8-Methyl-octadecane

Δ^{10} -*n*-Undecenoic acid was transformed through the acid chloride and the amide into Δ^{10} -*n*-undeceno nitrile in the same way as described for the synthesis of 3-methyl-octadecane.

Δ^{10} -*n*-undeceno nitrile. B. p. 135/15 mm, $n_D^{20} = 1.4442$, $d_4^{20} = 0.8443$. By the usual Grignards synthesis Δ^{10} -*n*-undeceno nitrile was transformed into 2-keto-*n*-dodecene-11. B. p. 120°/15 mm. M. p. + 2.5. This ketone has been prepared by Polgar and Robinson¹³, by the action of undecenoyl chloride on methylzinc iodide, they stated the b. p. as 114—115°/9 mm.

5.8 g 2-keto-*n*-dodecene-11 was slowly added to 6.7 g $\text{CH}_3\text{-(CH}_2)_5\text{-CH}_2\text{-Mg-Br}$ in a little ether, and the tertiary carbinol worked up as above.

$\text{C}_{19}\text{H}_{38}\text{O}$ (282.4) Calc.	C 80.735	H 13.57
Found	80.16, 80.36	13.52, 13.49

The 8-methyl-octadecane was prepared from 8-methyl-octadecene-17-ol-8 as usual.

Table 15. Dispersion of 8-methyl-octadecane.

$$d_4^{20} = 0.78595, \quad \lambda_0 = 887.07 \text{ \AA}, \quad R_{\lambda=\infty} = 88.109.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} calc.
6678.1	1.43838	89.687	89.692
5895.8	1.44098	90.149	90.149
5875.7	1.44110	90.171	90.164
5460.7	1.44291	90.492	90.497
5015.6	1.44563	90.974	90.954
4471.48	1.44983	91.716	91.719
4358.3	1.45089	91.903	91.917

9-Methyl-octadecane

Methyl *n*-nonyl ketone was isolated from rue oil by distillation and recrystallization. *n*-Octanol was prepared from caprylic acid ethyl ester according to the above-mentioned method of Bouveault-Blanc. Further, 1-brom-*n*-octane according to Org. Syntheses I p. 7. 9-Methyl-octadecanol-9 was prepared after the standard Grignard procedure from 1-brom-*n*-octane and methyl-*n*-nonyl-ketone.

$C_{19}H_{40}O$ (284.4) Calc.	C 80.21	H 14.17
Found	» 79.93, 79.76	» 14.16, 14.16

Table 16. Dispersion of 9-methyl-octadecanol-9.

$$d_4^{20} = 0.8355, \lambda_0 = 883.5 \text{ \AA}U, R_{\lambda-\infty} = 89.542.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} , calc.
6678.1	1.44814	91.124	91.137
5895.8	1.45085	91.601	91.599
5875.7	1.45099	91.626	91.613
5460.7	1.45281	91.945	91.948
5015.6	1.45559	92.433	92.409
4471.48	1.45981	93.171	93.179
4358.3	1.46092	93.365	93.379

The 9-methyl-octadecane was prepared from 9-methyl-octadecanol-9 in the usual way.

Table 17. Dispersion of 9-methyl-octadecane.

$$d_4^{20} = 0.78555, \lambda_0 = 884.1 \text{ \AA}U, R_{\lambda-\infty} = 88.087.$$

λ	n_{λ}^{20}	R_{λ} , obs.	R_{λ} , calc.
6678.1	1.43791	89.649	89.658
5895.8	1.44055	90.119	90.113
5875.7	1.44062	90.131	90.128
5460.7	1.44245	90.456	90.458
5015.6	1.44513 ₅	90.932	90.912
4471.48	1.44932	91.673	91.671
4358.3	1.45033	91.851	91.868

SUMMARY

For comparison with pristane the eight monomethyloctadecanes were synthesized. The densities and refractive indices of the methyloctadecanes approached very closely to those of pristane, the m. p. however fell between

— 16.5° and + 13.2° for the methyloctadecanes as against < -87° for pristane. As intermediate compounds in the synthesis of the methyloctadecanes the tertiary alcohols. 3-, 4-, 5-, 6- and 9-methyloctadecanols and the tertiary alcohols 7- and 8-methyloctadecene-17-ols were prepared. The physical constants including the dispersions of the new compounds are given.

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