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On the Determination of C-Methyl Groups in Aliphatic Long Chain Compounds

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The determination of methyl groups linked to carbon is often an important matter in connexion with structure determinations. The method originally described by Kuhn and Roth [1] and later modified by Wiesenberger [2] is satisfactory for most types of compounds. However, with aliphatic long chain compounds which have often to be analyzed in this laboratory difficulties are encountered with the method as originally described. The modification described by Ginger [3] has been found to give reasonably good results for saturated fatty acids and alcohols containing up to about 20 carbon atoms. In Ginger's method, the sample is dissolved in sulphuric acid, the solution cooled to room temperature, and the chromic acid solution added drop-wise until the oxidation begins. The solution is then cooled in ice-water and the bulk of the chromic acid oxidation solution added. The mixture is then refluxed for 90 minutes, and the acetic acid distilled off and titrated. When we used this procedure it was found to be essential that most of the sample was oxidized already on the drop-wise addition of the chromic acid solution. If during the later refluxing an appreciable amount of unchanged sample was present, fatty material crept up into the condenser and was thus withdrawn from further oxidation. Long chain hydrocarbons could not be analyzed using this procedure, because, if at all dissolved, they were immediately precipitated from the sulphuric acid solution when the chromic acid was added, and were therefore only attacked to a small extent. It was evident, therefore, that the oxidation conditions had to be changed if such compounds were to be analyzed. In particular, it appeared necessary to increase the degree of dispersion for compounds not soluble in sulphuric acid. The samples with oxidation solution were therefore sealed into glass tubes and the tubes shaken at an elevated temperature for a suitable time. After cooling, the tubes were opened, the contents washed out and the acetic acid formed distilled off and titrated.

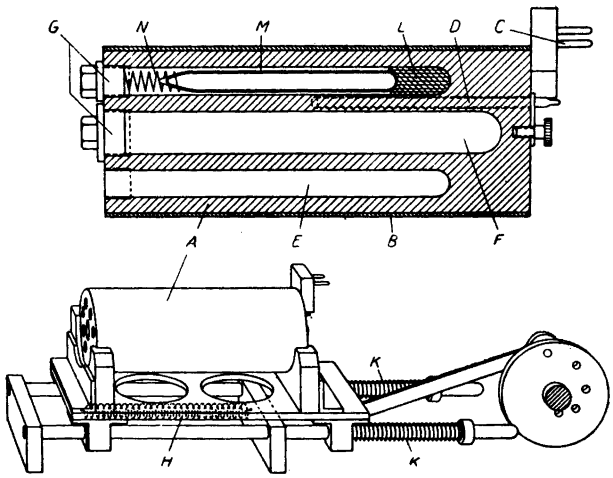

Fig. 1. Mechanical shaker. A = aluminum block, B = heater with asbestos insulation, C = plug connection for heater, D = iron-constantan thermocouple, E, F = bores for bombs, G = retaining plugs, L = cotton wool, N = spring keeping bomb M in position, H and K = springs.

To begin with we used the dilute oxidation solution used by Kuhn and Roth[1], and shook the sample at moderate speed at 120° C (procedure 1). The bombs were shaken for different lengths of time in order to determine the suitable reaction time. The results are shown in the diagrams (Figs. 4—13). With normal chain fatty acids with up to 20 carbon atoms reproducible diagrams were obtained, but with very long chain acids the reproducibility was not satisfactory. With long chain hydrocarbons such as *n*-hentriacontane (Fig. 13) the decomposition was incomplete even after a very long time of shaking. 12-Ketohentriacontane (Fig. 12) on the other hand decomposed very quickly, probably both because of higher solubility in concentrated sulphuric acid and because the carbon chain is readily broken off at the place of the keto group. The shape of the curve after the decomposition shows that the acetic acid formed is attacked only to a negligible degree by the oxidation solution. Analyses 1—6 in Table 1 were carried out following this procedure.

As very long chain hydrocarbons could not be satisfactorily analyzed in the manner just described we tried stronger oxidation solutions, higher temperatures, and more violent shaking in order to obtain a better decomposition of the samples. Stronger oxidation solution and higher temperatures increased, however, not only the rate of formation of acetic acid, but also the rate of its decomposition (Fig. 14). Only the higher rate of shaking had an entirely good

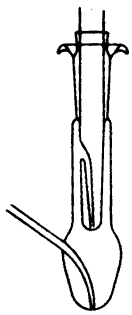

Fig. 2. Distillation flask according to Wiesenberger with sealed-in gas inlet tube.

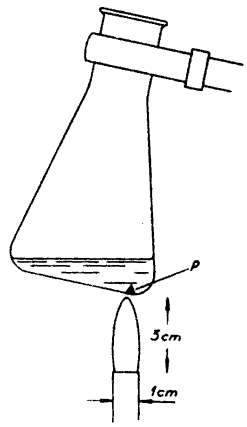

Fig. 3. Boiling the distilled acetic acid prior to titration. P = platinum tetraeder.

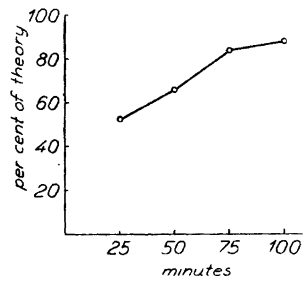

Fig. 4. Di-n-heptylacetic acid, procedure 1.

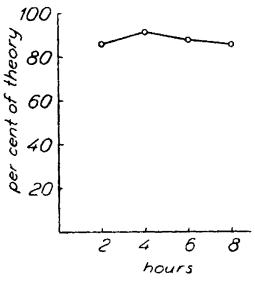

Fig. 5. Methyl 6-methyl-1,11-hendecandioate, procedure 1.

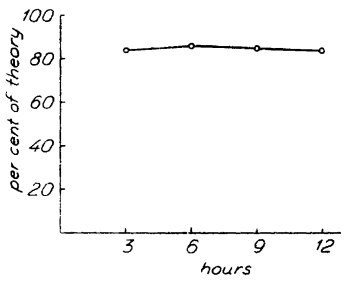

Fig. 6. 16-Methylheptadecanoic acid, procedure 1.

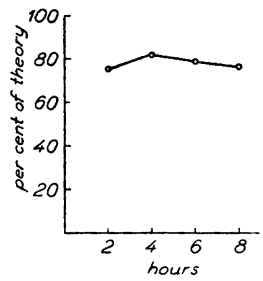

Fig. 7. Methyl 15-methylheptadecanoate, procedure 1.

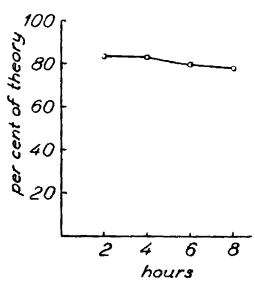

Fig. 8. Methyl 14-methyloctadecanoate, procedure 1.

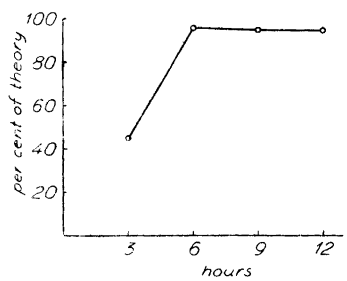

Fig. 9. 33-Methyltetratriacontanoic acid, procedure 1.

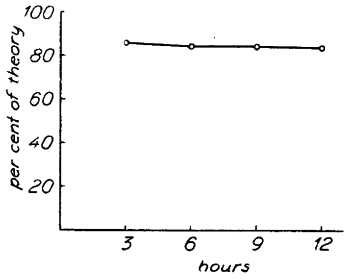

Fig. 10. n-*Eicosanoic acid, procedure 1.*

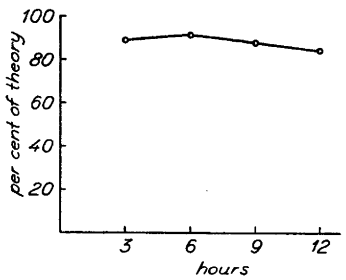

Fig. 11. n-*Hexacosanoic acid, procedure 1.*

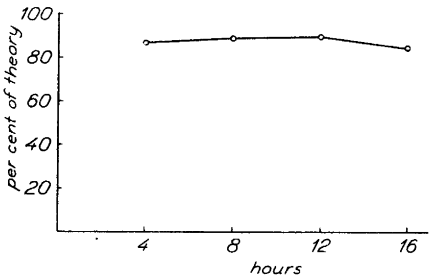

Fig. 12. 12-Ketohentricontane, procedure 1.

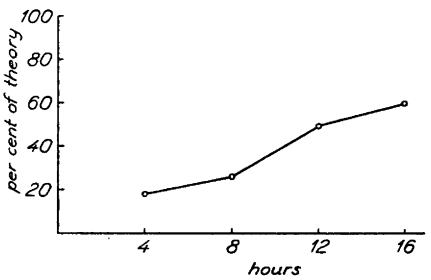

Fig. 13. n-*Hentriacontane, procedure 1.*

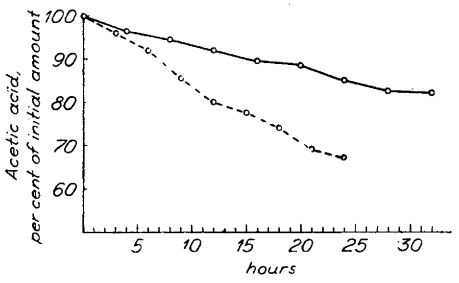

Fig. 14. Rate of destruction of acetic acid. Procedure 1 = full drawn line, procedure 2 = dashed line.

influence on the reaction, as the dispersion of the sample was increased, leading to an increase in the reaction surface. However, with the apparatus used it was not possible to increase the rate of shaking above the figures given for procedure 2 in the experimental part. It is possible that some special method of dispersion of the samples, *e.g.* ultrasound, would give still better results than we have obtained. The best results were obtained using the figures for solution, temperature and shaking given for procedure 2. After four hours shaking following this procedure all organic substance was destroyed and no

*Table 1. Analyses.**

Nr	Substance	CH_3 groups present	CH_3 groups possible to determine as acetic acid	$CH_3-(C)$ % Found	% Calcd	% of Theory	CH_3 groups found
1	*n*-Dodecanoic acid	1	1	6.27	7.52	83.4	0.83
2	—"—			6.25	7.52	83.2	0.83
3	—"—			6.26	7.52	83.3	0.83
4	Methyl 6-methyl-1,11-hendecanedioate			4.69	5.32	80.6	0.81
5	Ethyl azelate	2	2	11.98	12.30	97.4	1.95
6	—"—			11.98	12.30	97.4	1.95
7	*n*-Tetratriacontane	2	2	4.63	6.28	73.7	1.47
8	—"—			4.74	6.28	75.5	1.51
9	—"—			5.02	6.28	79.9	1.60
10	—"—			5.02	6.28	79.9	1.60
11	*n*-Nonatriacontane	2	2	4.12	5.48	75.2	1.54
12	—"—			4.08	5.48	74.5	1.49
13	*n*-Tetratetracontane	2	2	3.68	4.85	75.9	1.52
14	*n*-Hexacosanoic acid	1	1	2.84	3.79	74.9	0.75
15	—"—			2.84	3.79	74.9	0.75
16	14-Methylheptadecanoic acid	2	2	7.57	11.12	68.1	1.36
17	—"—			7.62	11.12	68.5	1.37
18	DL-9-Methyloctadecanoic acid	2	2	7.31	10.07	72.6	1.45
19	—"—			7.07	10.07	70.2	1.40
20	DL-4-Methylpentacosanoic acid	2	2	5.21	7.58	68.8	1.38
21	—"—			5.27	7.58	69.5	1.39
22	DL-5-Methylhexacosanoic acid	2	2	5.05	7.32	69.0	1.38
23	33-Methyltetratriacontanoic acid	2	1	2.40	2.87	83.6	0.84
24	—"—			2.38	2.87	82.9	0.83
25	—"—			2.06	2.87	69.1	0.69
26	Di-*n*-heptylacetic acid	2	2	7.92	10.00	79.2	1.58
27	—"—			8.12	10.00	81.2	1.62
28	DL-α-Methyl-α-ethylsuccinic acid	2	2	13.13	18.77	70.0	1.40
29	—"—			13.18	18.77	70.2	1.40
30	Ethyl β,β-dimethylglutarate	2	1	14.92	20.85	71.6	0.72
31	—"—			15.22	20.85	73.0	0.73

* In analysis 5 the time of shaking was 20 minutes, in analysis 6 one hour, and in all other analyses 4 hours.

Nr	Substance	CH_3 groups present	CH_3 groups possible to determine as acetic acid	$CH_3-(C)$ % Found	% Calcd	% of Theory	CH_3 groups found
32	α-Methyl-ω-phenoxipropyl-acetic acid	1	1	5.11	7.22	70.8	0.71
33	—"—			5.10	7.22	70.6	0.71
34	Methyl-*n*-dodecylacetic acid	2	2	9.08	12.40	73.2	1.46
35	—"—			9.13	12.40	73.6	1.47
36	Methyl hexadecane-1,16-dicarboxylate	0	—	0.06	0	—	0.01
37	—"—			0.06	0	—	0.01
38	Octatriacontane-1,38-dicarboxylic acid	0	—	0.29	0	—	0.12
39	—"—			0.14	0	—	0.06
40	—"—			0.36	0	—	0.15
41	—"—			0.38	0	—	0.16
42	9,30-Diketooctatriacontane-1,38-dicarboxylic acid	0	—	0.52	0	—	0.23
43	—"—			0.52	0	—	0.23
44	Mycocerosic acid *	not known	not known	9.98			3.33
45	—"—			9.98			3.33

* The sample of mycocerosic acid was kindly given by Professor R. J. Anderson, Yale University. All other compounds analyzed have been synthesized in this laboratory.

"wax" crept over during the distillation, as had occurred generally with the other procedures tried and after a shorter time of shaking. Even with this procedure the earlier part of the yield-time curves obtained with samples with very long chains were not well reproducible, but the results after the four hours of shaking of the samples were. Analyses 7—44 were carried out following this procedure.

EXPERIMENTAL

Weighing of the samples.

The samples are weighed into the Pyrex glass bombs, which have an inner diameter of 8—9 mm, an outer diameter of about 12 mm, and a length of 120—150 mm, using the weighing tube of Lieb and Krainick [4]. Liquid samples are weighed into small glass thimbles and thrown into the bomb. The weight of the samples was 15—30 mg in procedure 1 and 8—12 mg in procedure 2.

Oxidation of the samples.

5 ml of oxidation solution are pipetted into the bombs containing the samples, and the bombs are sealed off. In procedure 1 the oxidation solution is 4 normal with respect to chromic acid, in procedure 2 it is 5 normal. In both procedures 50 ml of concentrated sulphuric acid is mixed with 200 ml of the chromic acid solution. For the shaking a mechanical shaker (Fig. 1) is used. An aluminum block with openings for eight bombs and provided with a winding for electrical heating and a thermocouple for automatic temperature control is shaken along its long axis. In procedure 1 the temperature is 120° C, the shaking proceeds at a rate of 74 periods/min. and the length of the stroke is 10 cm. In procedure 2 the temperature is 135° C, and the rate of shaking 150 periods/min., the stroke being 10 cm.

Distillation of the acetic acid.

The bombs are carefully opened in the usual manner and the contents are washed over into the distillation apparatus. To begin with the apparatus of Kuhn and Roth [1] was used. Later the apparatus of Wiesenberger [2] was preferred as it was time-saving and gave more accurate results. It was necessary, however, to seal a side tube into the distillation flask (Fig. 2) and to lead a very feeble nitrogen stream through it, as this proved to be the only way to avoid bumping in our solutions. In all other respects the directions for the distillation given by Wiesenberger were followed. The distillation was found to require some experience in order to distil over the acetic acid quantitatively without getting any sulphuric acid into the distillate.

Titration of the acetic acid.

Pregl and Soltys [5], Friedrich and Rapoport [6], Kuhn and Roth [1], and Wiesenberger [2] report good results when the solution is boiled for a short time before the titration. Hurka [7,8], however, states that the results obtained are low as the boiling causes loss of acetic acid. It is somewhat surprising that none of the above authors says anything about the size of the flame used for the boiling. When the solution was boiled strongly with a large flame large losses occurred already after boiling for 4—5 seconds, in good agreement with the results of Hurka. When we boiled gently with a small flame only negligible losses occurred even after a boiling time of 20 seconds. In the present work a boiling time of 7 seconds was used. The flame was an ordinary Bunsen flame with a height of 3 cm. The flask was held somewhat inclined and a platinum tetraeder was used to avoid bumping (Fig. 3). After the boiling, the flask was immediately immersed in cold water and a small watch glass was placed upon

it. After standing in the water for exactly two minutes one drop of 1 % phenolphtalein solution was added and the solution quickly titrated to the first pink tinge remaining for 5 seconds. Blank titrations were carried out in order to compensate errors.

SUMMARY

The determination of C-methyl groups in aliphatic compounds of high molecular weight by the Kuhn-Roth method has been studied. By improvement in the oxidation conditions, including the use of a stronger oxidation solution, a higher temperature and dispersion of the sample by mechanical shaking, it has been found possible to get satisfactory results for aliphatic compounds of very high molecular weight. The results of the analysis of a large number of normal and branched chain compounds having up to 44 carbon atoms in the molecule are given.

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