CCXXV. SYNTHESIS AND CRYSTAL SPACINGS OF CERTAIN LONG-CHAIN PARAFFINS, KETONES AND SECONDARY ALCOHOLS.

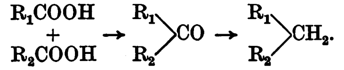
By STEPHEN HARVEY PIPER, ALBERT CHARLES CHIBNALL, SYDNEY JOHN HOPKINS, ALFRED POLLARD, JAMES ANDREW BUCHAN SMITH AND ERNEST FRANK WILLIAMS.

From the Wills Physical Laboratory, University of Bristol, and the Biochemical Department, Imperial College of Science and Technology, South Kensington.

(*Received October 31st, 1931.*)

INTRODUCTION.

It has long been known that plant waxes contain many substances, notably paraffins and long-chain primary alcohols, besides true waxes such as ceryl cerotate. Attention has been drawn recently to the possible path of metabolism in the plant of some of these substances by Channon and Chibnall [1929] who found that the wax fraction of cabbage leaves (which they refer to as the crude hydrocarbon) consisted chiefly of *n*-nonacosane and 15-nonacosanone. It was suggested by them that paraffins and ketones of this type might arise from the lower fatty acids by condensation and reduction in the following way:



$$\begin{matrix}R_1COOH\\+\\R_2COOH\end{matrix} \rightarrow \begin{matrix}R_1\\R_2\end{matrix}\!\!>CO \rightarrow \begin{matrix}R_1\\R_2\end{matrix}\!\!>CH_2.$$

Unfortunately, in the case of the cabbage ketone and paraffin, this postulates the presence of pentadecoic acid at some stage in the synthesis, and as acids containing odd numbers of carbon atoms have not yet been satisfactorily identified in nature, it was felt that the question of the immediate precursor of the ketone should be left over until further experimental evidence was available.

During the past two years we have been investigating the composition of the ethereal extract of numerous forage grasses and, as these all contain a high proportion of wax material, an opportunity has thus been afforded of obtaining more of the required evidence.

We were encouraged to undertake this work by the success attained by Francis, Piper and Malkin [1930] in their researches into the constitution of the long-chain fatty acids occurring in natural products. These authors obtained their standardising data from synthetic fatty acids of 14–26 carbon atoms, and from mixtures of these. They concluded that the identity of these fatty acids could only be established with certainty when the M.P. and 001 spacings of two crystal modifications were known. They were able to show quite definitely that the naturally occurring acids, usually referred to as arachidic, lignoceric, cerotic and montanic acids, were all mixtures of *n*-fatty acids. Furthermore, the crystal spacings obtained enabled them in certain favourable cases to deduce the probable composition of the mixture.

In the case of the plant waxes the X-ray method of analysis has again proved strikingly successful and the constitution of the main components, *e.g.* paraffins, ketones, primary alcohols, secondary alcohols and fatty acids, has been suggested with such certainty that confirmation by appropriate synthesis has been relatively easy. To attain this result we have had not only to perfect the methods of separating the various components of the waxes, but also to prepare highly pure synthetic products, especially paraffins, in order to have accurate standards of comparison. The present paper, which deals with these synthetic products and their X-ray analysis, is therefore a necessary forerunner to further papers dealing with the components of the various plant waxes.

EXPERIMENTAL.

Preparation of fatty acids.

(The M.P.'s in brackets refer to Francis, Piper and Malkin [1930].)

Kahlbaum's *myristic* and *palmitic* acids were recrystallised four times from large volumes of acetone; yield about 25 %, M.P. 54° and 63·0° respectively (54°, 63·1°).

Pentadecoic acid. 100 g. of Eastman Kodak acid (M.P. 48·5°) was fractionated five times by distillation *in vacuo* and after repeated crystallisation from light petroleum (B.P. under 40°) yielded 23 g. of pure acid; M.P. 52·5° (52·1°).

Stearic acid. Prepared by saponification of a specimen of ethyl stearate (iodine value 0·8) kindly supplied by Prof. Hilditch, which had been prepared by hydrogenation of ethyl oleate; M.P. 70·0° (70·1°).

Eicosanic acid. Prepared from Kahlbaum's erucic acid by heating with potassium hydroxide [Levene, West and Van der Scheer, 1915]. The crude acid was converted to the ethyl ester and fractionated at 206°/2·5 mm. After crystallisation from acetone the ester melted at 41–41·5° (41°) and the acid after repeated crystallisation from alcohol at 75–75·2° (75·2°).

Heneicosanic acid. Ethyl eicosanate was reduced to *n*-eicosanol by means of sodium in dry ethyl alcohol at 130°; yield 80 %, M.P. 65–65·5°. This was converted into the iodide (M.P. 41–42°) by heating with iodine and red phosphorus and hence to the nitrile by boiling overnight with potassium cyanide in absolute alcohol. Without isolation the nitrile was hydrolysed to heneicosanic acid by heating with excess of aqueous sodium hydroxide; yield 75 %; M.P. after repeated crystallisation from acetone and alcohol 74·2–74·6° (75·2).

Synthesis of ketones.

Symmetrical ketones. These have recently been prepared on a large scale in excellent yield by Grün, Ulbrich and Krczil [1926] who heated the requisite fatty acids in an iron vessel. In the present research the method of Gluud [1919] was first tried, as it seemed more applicable to small quantities of material. The barium soaps of the fatty acids were heated in a hard glass retort under reduced pressure, and the ketone, which slowly distilled over, was crystallised twice from alcohol. 12-Tricosanone (laurone), 15-nonacosanone and 16-hentriacontanone (palmitone) were prepared in this way in yields of 50–60 %. It was later found that improved yields could be obtained by a slight modification of the method of Grün *et al.* as follows.

Myristic acid (15 g.) was heated in a tall hard glass vessel to 285°. A loosely fitting sheet iron ring pierced with numerous holes had been previously placed in the vessel and was of such height that it was just covered by the molten acid. The melt was stirred by a glass paddle rotating within the ring, and after about 2 hours there was a sudden evolution of gas, with increase in viscosity of the liquid and considerable frothing. Heating was continued for a further 2 hours, when evolution of gas ceased. The melt was poured out of the tubes, cooled and then extracted with hot 95 % alcohol. The yellow solution was decolorised with charcoal, and on cooling the 14-heptacosanone (myristone) crystallised out. One recrystallisation from hot alcohol was sufficient to give a pure product; yield 9·7 g. or 75 %. 18-Pentatriacontanone (stearone) was also prepared by this method, the reaction temperature being 300–305°. The melting-points of these ketones and their oximes were in agreement with those of Grün *et al.* [1926] and of Channon and Chibnall [1929]. The oxime of 15-nonacosanone melted at 52–53°.

The following three unsymmetrical ketones were synthesised by the method used by Channon and Chibnall [1929] for the synthesis of 14-nonacosanone which is based on the synthesis of 6-ketostearic acid by Robinson and Robinson [1925]. The oxime of 14-nonacosanone has since been prepared; M.P. 45·5–46°.

12-Nonacosanone, $CH_3.(CH_2)_{10}.CO.(CH_2)_{16}.CH_3$. Ethyl palmitate, B.P. 152–155°/1 mm., was reduced with sodium in dry ethyl alcohol to *n*-hexadecanol, which was purified by distillation at 153–156°/1 mm., M.P. 50–51°. This was converted to the iodide by heating with iodine and red phosphorus. Sodium (5·5 g.) was dissolved in 90 cc. of absolute alcohol, ethyl acetoacetate (47 g.) added and finally *n*-hexadecyl iodide (82 g.). The mixture was boiled for 5½ hours, poured into 1500 cc. of water and the resulting ethyl 2-acetyl-*n*-octadecoate, $CH_3.(CH_2)_{15}.CHAc.CO_2.Et$, extracted with ether. It was fractionated twice and the fraction boiling at 189–195°/1·5 mm. collected; yield 56 g. (Found: C, 74·3; H, 11·8. $C_{22}H_{42}O_3$ requires C, 74·6; H, 11·9 %.) This ester (56 g.), dissolved in 300 cc. dry ether, was added to emulsified sodium (3·5 g.) suspended in 300 cc. dry ether and the mixture warmed until the sodium had dissolved. The mixture was then cooled on ice and dodecoyl chloride

(37·7 g.) in 80 cc. dry ether added. After standing for one hour the mixture was boiled for 10 minutes, cooled, the sodium chloride removed by washing with water and the ether removed by evaporation. The resulting oily 12-keto-13-acetyl-13-carbethoxy-*n*-nonacosane was dissolved without purification in 1400 cc. absolute alcohol. 5 % aqueous potassium hydroxide was then added until there was a slight turbidity and the mixture kept 4 days. Sufficient strong potassium hydroxide was then added to make the concentration 5 % and the solution boiled for 3 hours. The alcohol was evaporated and the solid residue extracted 6 times with hot acetone. The extracts on cooling deposited crystals, which were dissolved in light petroleum; the filtered solution was concentrated, and treated with two volumes of acetone. 12-Nonacosanone (20 g.) was precipitated. It was crystallised from 95 % alcohol (charcoal), M.P. 74·5°. (Found: C, 82·4; H, 13·3. $C_{29}H_{58}O$ requires C, 82·4; H, 13·8 %.) *Oxime*, M.P. 47–47·5°.

10-Nonacosanone, $CH_3.(CH_2)_8.CO.(CH_2)_{18}.CH_3$. By the method given above sodium (1 g.), alcohol (16 cc.), ethyl acetoacetate (7·5 g.) and *n*-octyl iodide (10 g.) gave 5·7 g. of ethyl 2-acetyl-*n*-decoate, a colourless oil, B.P. 140–141°/5 mm. Eicosanoyl chloride (6·4 g.) in dry ether (25 cc.) was added to ethyl sodio-2-acetyl-*n*-decoate (5·14 g.) in dry ether (25 cc.). The condensation product was saponified as before and yielded 2·4 g. of 10-nonacosanone. Recrystallised from light petroleum (B.P. 40–60°) it melted at 74·3–74·8°. (Found: C, 82·6; H, 13·8. $C_{29}H_{58}O$ requires C, 82·4; H, 13·8 %.) *Oxime*, M.P. 49·5–50°.

9-Nonacosanone, $CH_3.(CH_2)_7.CO.(CH_2)_{19}.CH_3$. Sodium (1 g.), alcohol (16 cc.), ethyl acetoacetate (7·5 g.) and *n*-heptyl iodide (10 g.) gave 6·3 g. of ethyl 2-acetyl-*n*-nonoate, a colourless oil, B.P. 122°/2 mm. Ethyl sodio-2-acetyl-*n*-nonoate (4·6 g.) condensed with heneicosanoyl chloride (6·3 g.) in dry ether yielded 2·2 g. of 9-nonacosanone. Recrystallised twice from light petroleum it melted at 73·5–74·2°. (Found: C, 82·2; H, 13·9. $C_{29}H_{58}O$ requires C, 82·4; H, 13·8 %.) *Oxime*, M.P. 48·5–49°.

All these long-chain ketones are fairly soluble in cold and very readily soluble in hot chloroform, benzene and xylene; slightly soluble in cold ethyl acetate, light petroleum (40–60°) and carbon disulphide; and almost insoluble in cold but fairly soluble in boiling acetone, ethyl and methyl alcohol. The oximes are readily soluble in cold light petroleum and in acetone-ether mixture.

Synthesis of secondary alcohols.

These were prepared in the usual way by reduction of the ketones. The ketone (1 g.) was dissolved in boiling amyl alcohol (40 cc.) and sodium (5 g.) slowly added. After 2 hours the mixture was cooled and washed with dilute hydrochloric acid and with water. The solvent was removed under reduced pressure and the residue recrystallised from alcohol (charcoal) and then from light petroleum (B.P. 40–60°). It was sometimes necessary to repeat the reduction. The melting-points (Table VI) of the symmetrical alcohols confirm those of Grün *et al.* [1926]. The following have not previously been prepared. *15-Nonacosanol*, M.P. 83·6–83·8°, S.P.[1] 83°; *acetate* M.P. 50·5–51°. *14-Nonacosanol*, M.P. 79–79·3°, S.P. 78·4°; *acetate* M.P. 41–42°. *12-Nonacosanol*, M.P. 74–74·5°, S.P. 73°; *acetate* M.P. 44–45°. *10-Nonacosanol*, M.P. 74·8–75°, S.P. 74·2°; *acetate* M.P. 45–45·5°. *9-Nonacosanol*, M.P. 75·3–75·6°, S.P. 74·8°; *acetate* M.P. 44·5–45°.

The alcohols have similar solubilities to the ketones, but are markedly less soluble in cold solvents such as low-boiling petroleum.

Synthesis of higher paraffins.

The paraffins with an odd number of carbon atoms were synthesised by Clemmensen reduction of the corresponding ketones. The following synthesis of *n*-nonacosane, which has not hitherto been prepared, will illustrate the method employed.

n-*Nonacosane.* Zinc wool (30 g.) was amalgamated by allowing to stand in 5 % aqueous mercuric chloride for one hour. It was washed and placed in a flask fitted with a reflux condenser together with 15-nonacosanone (2 g.) and 200 cc. of a mixture of equal volumes of concentrated hydrochloric acid and alcohol saturated with dry hydrogen chloride. The mixture was then boiled until evolution of hydrogen slackened, when the flask was cooled and the aqueous alcohol poured off. Fresh acid mixture was added as many times as was necessary to dissolve all the zinc. A further 20 g. was then added and the operation repeated. The final product was washed with water and recrystallised from alcohol (charcoal). It melted at 62·7–63·0°, and analysis showed it to be a hydrocarbon. (Found: C, 85·2; H, 14·8. $C_{29}H_{60}$ requires C, 85·2; H, 14·8 %.) Paraffins prepared in this way were used in the earlier X-ray experiments, but the pictures obtained were inferior to those of natural paraffins. After various methods of purification had been tried it was found that treatment with sulphuric acid was the most effective. The paraffin was heated with about 6–8 volumes of concentrated sulphuric acid in a test-tube immersed in an oil-bath at 130° for 2 hours. Considerable blackening of the acid occurred. The tube was removed from the bath, the paraffin melt on the surface of the acid allowed to set, and the acid drawn off. Fresh acid was added and the tube replaced. This operation was repeated two or three times if necessary, depending on the amount of charring that occurred. The paraffin was washed repeatedly with hot water, and crystallised from 95 % alcohol (charcoal). The purified product was again treated with concentrated sulphuric acid, when it was usually found that a little darkening still occurred. The treatment was repeated until a sample of sulphuric acid which had remained in contact with the paraffin at 130° for 2 hours showed no darkening. In all cases this treatment raised the melting-point of the paraffin about 0·5°. There was usually a loss during purification of 10–20 %, due to the solubility of the paraffin in the acid and to the

---

[1] S.P. signifies setting-point.

decomposition of olefines formed during the reduction. (Before treatment with sulphuric acid the *n*-nonacosane had iodine value 1·3 and *n*-pentatriacontane 2·6.) We have proved by appropriate experiments that ketones and alcohols are also quantitatively removed by this treatment. The following are in general agreement with Grün *et al.* [1926] and Kraft [1882]: n-*heptacosane*, M.P. 59·0–59·2°, S.P. 58·5°; n-*hentriacontane*, M.P. 67·6–67·8°, S.P. 67·3°; n-*pentatriacontane*, M.P. 74·4–74·6°, S.P. 74·3°. An earlier sample of *n*-pentatriacontane prepared from another sample of stearic acid, which was thought at the time to be pure, gave the same M.P. (74·6°) but a lower S.P. (74·0°). The X-ray picture was also inferior. This sample was the one used by Garner *et al.* [1931].

The following paraffins were synthesised by the method of Gascard [1921].

n-*Octacosane.* This paraffin has not previously been synthesised. A sample of *n*-tetradecanol was kindly supplied by Prof. Garner. It had been twice distilled, then recrystallised four times from alcohol and finally distilled, M.P. 38–38·5°, S.P. 37·7°. It was converted into the iodide (2·17 g.) which was boiled in sulphur-free xylene (70 cc.) with sodium (0·2 g.) for 3 hours. The cooled solution was washed with water, evaporated to 10 cc. and treated with two volumes of alcohol to precipitate the paraffin (0·54 g. or 36 %). The first treatment with sulphuric acid for 4 hours at 130° caused a little blackening of the acid, the second none at all, M.P. 61·4–61·5°, S.P. 61·1°. This paraffin was also prepared by the method of Backmann and Clark [1927]. Tetradecyl iodide (2·46 g.) was heated at 150° for 2 hours and sodium (1·3 g.) added slowly in small pieces with vigorous stirring. The yield after treatment with sulphuric acid was 70 % of theory. The X-ray picture showed that this preparation was inferior to the former, although the M.P. and S.P. were the same.

n-*Dotriacontane.* *n*-Hexadecyl iodide (1·13 g.) prepared from synthetic *n*-hexadecanol (p. 2074) was boiled in sulphur-free xylene (50 cc.) with sodium (0·2 g.) for 4 hours and the paraffin treated as before; yield 0·16 g., M.P. 69·5–69·7°, S.P. 69·3°. The paraffin prepared from purified natural cetyl alcohol (M.P. 49°) had M.P. 70·3–70·7°, confirming that of Gascard [1921], 70·5°. Kraft [1882] pointed out that natural cetyl alcohol contained some 4–5 % of octadecyl alcohol; the M.P. of the derived paraffin confirms this.

n-*Hexatriacontane.* This was prepared from *n*-octadecyl iodide (0·5 g.) kindly supplied by Dr Malkin, and sodium (0·1 g.) in boiling xylene as before, M.P. 75·7–75·9°, S.P. 75·4°. (Gascard [1921], M.P. 76°.)

The following paraffins were kindly supplied by Prof. Garner [*cf.* Garner, van Bibber and King, 1931]. They had been prepared by electrolysis of the respective fatty acids [Peterson, 1906] and were purified by treatment with sulphuric acid.

n-*Hexacosane*, M.P. 56·4–56·6°, S.P. 56·1° (Gascard [1921], M.P. 56·5°; Garner *et al.* [1931], S.P. 56·1°).

n-*Triacontane*, M.P. 65·6–65·8°, S.P. 65·5° (Gascard [1921], M.P. 65·6–66°; Garner *et al.* [1931], S.P. 65·6°). X-ray analysis showed that this paraffin was not pure, although the M.P. seems correct.

n-*Tetratriacontane*, M.P. 72·5–72·8, S.P. 72·4 (Gascard [1921], M.P. 73·2°; Garner *et al.* [1931], S.P. 72·4°).

These long-chain paraffins are freely soluble at room temperature in low-boiling light petroleum and carbon disulphide [*cf.* Brooks, 1922, p. 581 for solubilities of paraffin wax] but the solubility decreases rapidly with lowering of temperature, and with increase of molecular weight.

For the carbon and hydrogen analyses of the substances mentioned in this paper the usual micro-apparatus of Pregl [1924] with the phosphorus pentoxide absorption tube of Drew and Porter [1928] was first used. The carbon, especially in the case of paraffins, was frequently low, possibly due to the volatility of the substances at high temperature. To obtain accurate and reproducible results it was necessary to modify the apparatus and usual procedure in the following way. The length of the copper oxide column in the tube was increased from 140 mm. as recommended by Pregl to 160 mm., the gauze round that part of the tube containing this oxide being heated to a bright red heat. The actual burning of the compound was carried out rather more slowly than is necessary for the average substance, 70 cc. of oxygen being passed in for this purpose at the rate of not more than 3 cc. per minute, this being followed for "sweeping out" purposes by 100 cc. of air at 4–5 cc. per minute.

Measurement of the crystal spacings.

There are now available large numbers of measurements of the 001 spacings of various long-chain compounds. For any homologous series linear relationships exist between these spacings and the number of carbon atoms in the chain. It is obvious that the spacings of a series once measured will serve as a means of identification. Original work on synthetic paraffins has been carried out by Müller and Savile [1925, 1928, 1930] and Piper *et al.* [1925].

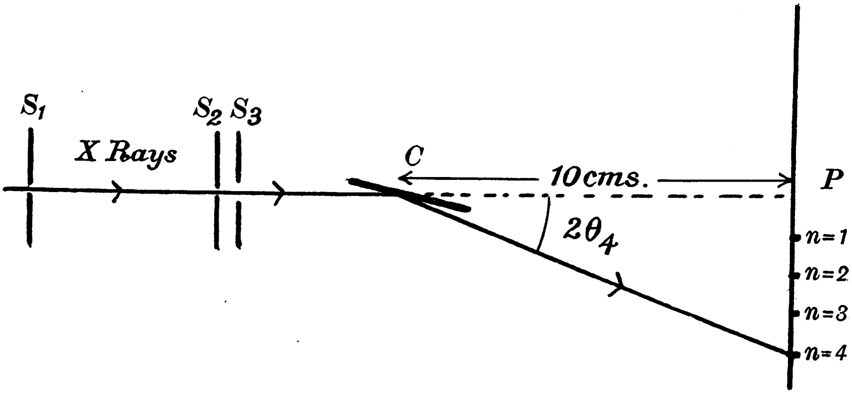


Fig. 1.

Although the technique has often been described it will be convenient to outline the procedure. The substances all crystallise in flakes, and the required planes lie parallel to the flake surfaces. A very thin layer is pressed on to a plate-glass mount to give a surface of about 1 cm. by 5 mm. wide. The plate is held vertically in a geometric clamp on the spectrograph in such a way that the surface is in the axis of rotation of the table. A narrow beam of X-rays from a Shearer tube of copper anticathode, filtered by a nickel foil, passes through the slits S_1, S_2, S_3, Fig. 1, and falls on the crystals at grazing incidence. The crystal is rocked to and fro through 14° by a cam mechanism, and the radiation it reflects is received on a photographic plate placed 10 cm. away at P. This plate is adjustable for height and is provided with a lead screen allowing successive exposures of strips 5 mm. deep. As many as 16 exposures can be made on the same plate. An exposure takes 30 minutes after which the crystal is turned through 180° and a second exposure is made on the other side. Reflection only occurs at glancing angles θ_1, θ_2, θ_3, *etc.*, determined by the Bragg equation

$$n\lambda = 2d \sin \theta_n,$$

where λ is the wave-length, $n = 1, 2, 3$, *etc.*, the order of the reflection, and d the crystal spacing. With good material and chains of 20 or more carbon atoms 9 or 10 orders can be obtained between $\theta = 0$ and 14°. The trace on the plate consists of a series of lines approximately equally spaced and decreasing in intensity with increasing order, and, since $\sin \theta$ is inversely proportional to d, the lines on the plate are close together for large spacings (long chains) and more widely separated for short chains. The values of θ for as many orders as possible are found, and d calculated. It has to be remembered that the actual position of the reflecting surface is indeterminate, but in front of the axis of rotation of the table. The correction to be applied decreases with increasing order and must be found by successive approximations from the value of d obtained from a high order. As a result the larger the number of orders measured the greater the accuracy attainable.

The spacing of a given specimen of paraffin can, with the apparatus in use, be measured to an accuracy of 0·1 %. However, we have found that different synthetic preparations of the same paraffin, apparently equally pure, and made by the same process, sometimes do not give spacings agreeing to less than 0·2 %. A repetition of the spacings to an accuracy of 0·1 % can probably only be obtained by working with single crystals, and we have not found it profitable to attempt more than 0·25 % except for the synthetic standards.

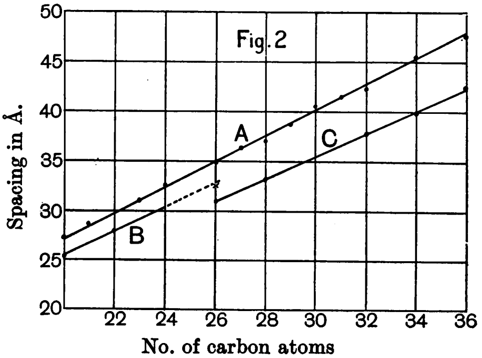
A spacing-carbon atoms graph for the paraffins is shown in Fig. 2. The points for 20, 21 and 24 carbon atoms are taken from Müller and Savile [1930], the higher members have been freshly determined from the material whose preparation has been described and are shown in Table I. Fig. 2 shows that the paraffins are polymorphous; *n*-hexacosane, for instance, may crystallise in two forms having spacings 34·95 and 31 Å. The particular crystal form adopted depends upon temperature, the length of the chain, and the degree of purity of the specimen.

Odd number paraffins of 11 or more carbon atoms normally crystallise with the chain axis vertical to the 001 planes, and the planar spacing is a direct measure of the length of the molecule. Even number paraffins of 18 or more atoms crystallise in this form at temperatures near the melting-point. These spacings fall on line *A* of Fig. 2. Even number paraffins up to 24 atoms, at normal temperatures, crystallise with the chain axis inclined at a constant angle to the planes. The 001 spacings of this *B* modification are shorter than those of the *A* form and lie on another straight line. *B* crystals are converted to *A* at temperatures very close to the melting-point and resume the *B* form on cooling. Odd number chains of 9 or less also adopt the *B* form under similar conditions [Müller and Savile, 1930].

Table I. *Melting-points and crystal spacings of the paraffins.*

Paraffin	First transition-point on heating	Second transition-point on heating	M.P.	S.P.	First transition-point on cooling	Second transition-point on cooling	Series No.	Crystal spacing in Å. *A*	*B*	*C*	
$C_{26}H_{54}$	51·5–52°	56·0°	56·4–56·6°	56·1°	55·5°	48·3°	C 67	34·95	32·6	31	*B* has only appeared in natural products
$C_{27}H_{56}$	52·8–53°	58·8–58·9°	59·0–59·1°	58·5°	58°	51°	C 22, 23	36·38	—	—	
$C_{28}H_{58}$	57–57·4°	61·2°	61·4–61·5°	61·1°	60·4°	54°	C 114	37	—	33·25	
$C_{29}H_{60}$	57·3–57·5°	63·2°	63·4–63·6°	63·2°	62·2°	55·8°	C 26	38·68	—	—	
$C_{30}H_{62}$	59–59·5°	65–65·3°	65·6–65·8°	65·4°	64·3°	58°	C 69	40·5	—	Not observed	Impure
$C_{31}H_{64}$	62–62·5°	67·2–67·4°	67·6–67·8°	67·3°	66·2°	61·8°	C 125	41·55	—	—	
$C_{32}H_{66}$	65·2–65·4°	69·2–69·4°	69·5–69·7°	69·2°	68·6°	63·9°	C 122	42·33	—	37·8	
$C_{34}H_{70}$	69·2–69·4°	72·2°	72·6–72·8°	72·4°	71·4°	68·5°	C 70, 71	45·5	—	39·86	
$C_{35}H_{72}$	71·8–72°	74·0°	74·4–74·6°	74·1°	73·0°	70·5°	C 28	46·64	—	—	
$C_{36}H_{74}$	73·9–74·1°	75·1–75·3°	75·7–75·9°	75·6°	74·6°	72·5°	B 121	47·5	—	42·33	

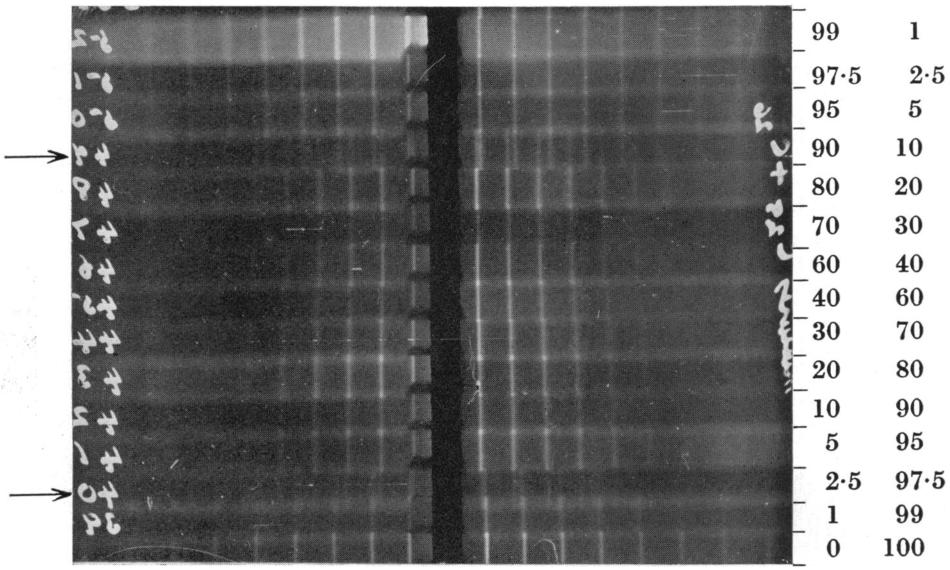
The *A* spacings of the even number paraffins are not so accurate as the remaining measurements. They only occur at temperatures near the M.P. for good crystals, and it is difficult to measure more than three orders.



× = This spacing has not been observed in synthetic hexacosane.

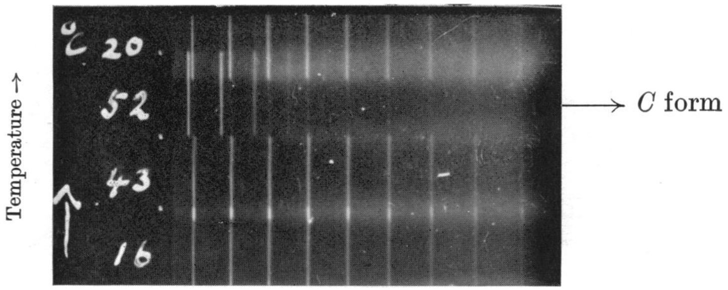
The paraffins that have been most important in this work have 26 or more carbon atoms. If pure these crystallise stably in yet a third modification, *C* of Fig. 2. This form is characterised by a larger tilt of the molecular axis and, of course, by still shorter spacings [Piper and Malkin, 1930]. *n*-Hexacosane can apparently appear in all three forms. We are mainly concerned with spacings lying on the *A* and *C* lines, these are given in Table I. *C* form is converted to *A* at a temperature about 5° below the M.P. Of our specimens hexacosane

Fig. 1.



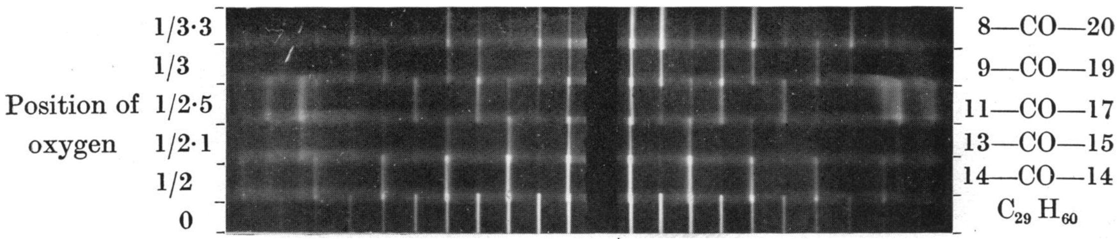
Synthetic mixtures. Changes from *A* to *C* form marked by arrows.

Fig. 2.



Temperature change in *n*-hexacosane.

Fig. 3.

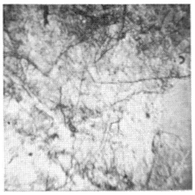


Shearer intensity variation in some nonacosanones.

Fig. 4.

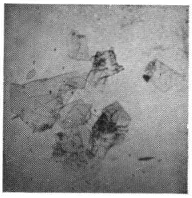
Tetratriacontane.
Polarized light.

Fig. 5.



Triacontane.

Fig. 6.



Tetratriacontane.

Unpolarised light.

reverted to *C* on cooling, the others did not, and the reverse change, if it occurs, must be extremely slow at room temperatures. A photograph of hexacosane in both forms is given in Plate VIII, Fig. 2.

The melting- and transition-points of the paraffins.

If the melting-point of a paraffin is carefully determined, as described below, it is possible to obtain not only the true melting- and setting-points but also to determine two transition-temperatures at which a change in crystalline form occurs. The lower of these transition-temperatures is markedly affected by impurities and, in certain cases, is a much more useful guide to the purity of the paraffin than the melting- or setting-point itself. It is necessary therefore to describe in some detail our method of taking these temperatures.

The melting-point apparatus was of the usual glass bulb type and held 80 cc. of sulphuric acid. It was fitted with a standard short stem thermometer which had a spherical bulb of diameter 4 mm. and was graduated in 0·2°. The acid in the bulb was not stirred, and, by using a small flame, it was possible with care to repeat a melting-point with an error of ± 0·1°. The material was first melted into open capillary tubes of outside diameter about 1 mm. The depth of the melt, which, after sealing, was jerked sharply to the bottom of the tube, was about 2 mm. All melting-points are corrected.

The following observations for *n*-nonacosane will illustrate the method of taking melting-points. The melting-point tube lying alongside the bulb of the thermometer is viewed through a lens giving a magnification of × 3. At room temperature the material in the tube appears as a white opaque crystalline mass. The temperature is raised rapidly to about 55° and then more slowly (1° per minute). At 57·3–57·5° a transition occurs. The crystalline structure disappears, the material becomes colourless, and an air gap down the centre, in the form of an attenuated inverted cone, is revealed. The temperature is again raised fairly rapidly to 63° and then, still more slowly than before, through the final melting-point. At 63·2° the material once again becomes opaque and the cone structure is no longer seen. Fusion takes place at 63·4–63·6° and the temperature is held within these limits until all the material is melted. The temperature is then allowed slowly to fall; at 63·2° long needles appear throughout the whole molten mass. The heating flame is then withdrawn so that the bath cools a little more rapidly. Between 62·5° and 62·2° the crystalline structure disappears. Contraction during the change of state leads to the formation of the inverted cone-shaped air gap, the rest of the material becoming clear and colourless. At 56° transition takes place quite suddenly to the original white crystalline and opaque form, which is the stable one at room temperatures.

In the case of the longer-chain paraffins, $C_{34}H_{70}$, $C_{35}H_{72}$ and $C_{36}H_{74}$, the transitions are much less marked, and can only be observed if the previous cooling of the material in the tube has been very slow. It is the usual practice in our laboratory to place the tube, when first made, in a bath which is at a temperature already above the melting-point, and to take the setting- and transition-points on cooling. The melting- and transition-points on heating are taken later. The time required to make the six observations is about 25–30 minutes. To eliminate the personal factor all the melting- and transition-points recorded in this and the two following papers were taken by one observer (A. C. C.).

The melting-, setting- and transition-points of the paraffins between $C_{26}H_{54}$ and $C_{36}H_{74}$ are given in Table I. As we believe that all these compounds (except $C_{30}H_{62}$) are pure the following deductions can be made.

Melting-points. The series $C_{26}H_{54}$ to $C_{32}H_{66}$ lie on a smooth curve (Fig. 3). There is evidence of alternation between $C_{34}H_{70}$, $C_{35}H_{72}$ and $C_{36}H_{74}$. We are therefore not entirely in agreement with the conclusions of Hildebrand and Wachter [1929] who adopted the somewhat dubious course of plotting all the values to be found in the literature, which assumes that all the products have been made from fatty acids of equal purity. The M.P. determined by our method may be some 0·5–0·7° lower than that given by the more usual method in which the temperature of a stirred bath is raised from 3° to 6° per minute. Even so we are unable to explain the high values recorded by Levene, West and Van der Scheer [1915].

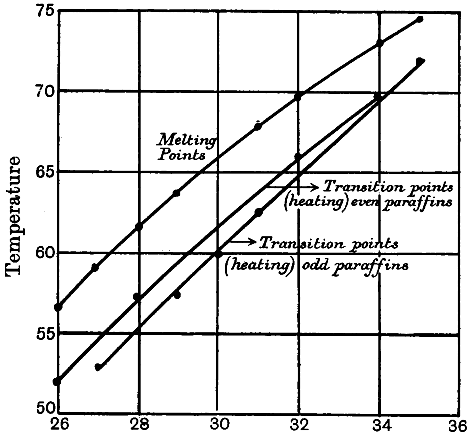


Fig. 3. Melting- and transition-points.

Setting-points. Supercooling was never observed in the case of pure paraffins or mixtures of pure paraffins, and it is unnecessary to leave a nucleus.

First transition-point. Alternations between odd and even numbered chains are observed in the change from the stable low temperature crystalline form to the colourless glass. The temperatures recorded are few in number, but give satisfactorily concordant results. The values are plotted in Fig. 3. Both odd and even series show a convergence of melting- and transition-points as the chain length increases. Particularly interesting is the position of the transition-temperature of triacontane which falls on the odd number paraffin line. This particular specimen of triacontane will only crystallise with a vertical chain (the *A* form), and, in view of the fact that this is the crystal modification adopted by the odd number paraffins, its position among them appears normal. The even number paraffins crystallising normally with a tilted molecule show, as would be expected (since for them the vertical chain is a less stable form), higher transition-temperatures (Fig. 3). All transition-temperatures on cooling lie on one smooth curve.

Second transition-point. This is often difficult to observe and as it is not apparently affected by impurities it will not be quoted in the tables dealing with mixtures and in further publications. In the future, "transition-point" is to be taken as referring to the first transition mentioned above.

Crystal forms of paraffins.

Microscopic investigation confirms the melting-point data, namely that all the longer paraffins have a transition-point involving a structural change. Plate VIII, Figs. 6 and 4, shows the appearance of some very pure *n*-tetratriacontane under the microscope and between crossed Nicols. The crystals, which are in the *C* modification, appear as rhombs of acute angle 73° and show very clear straight cleavages. There is also a marked double refraction effect noticeable. Plate VIII, Fig. 5 is a specimen of *n*-triacontane in unpolarised light; it is not quite pure and does not display such marked cleavages, also the crystals are very much smaller. They show no marked effect between crossed Nicols. These crystals are in the *A* form. Plate VIII, Figs. 5 and 6 should be compared as showing the difference in appearance in unpolarised light of a fair and a very good preparation of an even number paraffin. Odd number paraffins never take the *C* form, but Müller and Savile [1928] has found single crystals in the *A* form with an acute angle of 66°. The odd number paraffins examined had no definite optic axes, but the crystals were extremely minute and in a confused mass, and there was indication of a slight restoration of the light through crossed Nicols. If the crystals are placed in a heating stage they will all be found to undergo a structural change about 5° below the M.P. both on heating and cooling. A crystal in the *C* form breaks up at this temperature and does not appear to recrystallise with its previous optical properties.

The apparent lack of concordance between these observations and the X-ray data, which indicate transitions only for even number paraffins, is due to the fact that the latter, in our case, deal only with one crystal dimension. The reversible change common to all appears to correspond with one observed by Müller and Savile [1930] near the M.P., and presumably involves a change of cross-section of the cell without affecting the molecular tilt. Such a change should not affect the spacings we photograph. But with the longer even members there is, in addition, a change in tilt at or near this temperature which does not always reverse on cooling, and this change involves an increase in the 001 spacing. A very similar temperature change is found with even number fatty acids, Piper *et al.* [1926].

The heats of crystallisation of the paraffins of 22, 26, 30, 34 and 35 carbon atoms have been measured by Garner, van Bibber and King [1931]. Temperature transitions were found for all these at temperatures about 5° below the M.P. Now it is noticeable that while the heats of transition of 22, 26 and 34 increase uniformly with chain length, the values for 30 and 35 are lower. Prof. Garner kindly allowed us to photograph his material and we found that 22, 26 and 34 were in *B* or *C* form whilst 30 and, of course, 35, were in the *A* modification. Thus both paraffins with a low heat of transition had vertical chains and the other three tilted chains. The spacing and M.P. of triacontane were both high, which suggests contamination by not less than 2·5 % of a longer-chain paraffin. Impurity may not have a marked direct effect on the heat of transition, but it tends to force an even number paraffin to crystallise with a vertical chain, and it is plausible to suggest that part at least of the defect in heat of transition for triacontane represents the difference in energy between the *C* and *A* forms of this paraffin. *C* will, of course, have slightly less energy. Throughout their curves there is no indication of a double break, so the change in tilt occurs simultaneously with the other structural change.

Spacings of mixtures of paraffins.

Assuming that the anomalous results obtained with *n*-triacontane (low heat of transition, anomalous transition temperature, no *C* spacing) were due to lack of purity, we attempted a systematic investigation of the crystallisation of mixed paraffins. These were prepared in the following way. Benzene solutions of known strength were made for each paraffin. To prepare the necessary mixture the requisite aliquot of each benzene solution was pipetted into a small beaker, the benzene removed almost completely on a water-bath, and two volumes of hot alcohol were added. The paraffin mixture crystallises out almost quantitatively on cooling. Since the paraffins have a small residual solubility in the mixed solvent it follows that when one is added only in small amount, *e.g.* 1 %, the mixed crystals may actually contain a little less than this proportion. It is known from recent work on the separation of mixed paraffins by fractional crystallisation that temperature of crystallisation can slightly affect the composition. The spacings for binary mixtures whose chain-lengths differ by one or two carbon atoms are shown in Tables II–V and Figs. 4–7.

Only one 001 spacing occurs for all mixtures unless the components are separated by at least 4 carbon atoms. We commenced with two odd number chains (29 and 31) as the results are not confused with alternative crystal forms. A 1 % addition of 31 in 29 raises the spacing by about 1 %. The spacing continues to rise fairly uniformly with the amount of 31 until at equimolar proportions it is 41·2, approximately the spacing of the *n*-hentriacontane used. The mixed spacing continues to rise to a maximum when 97·5 % of the higher paraffin is present and then falls to that of pure *n*-hentriacontane. This behaviour appears general for A form spacings; except in one case paraffin impurity up to 1 % increases the spacing whether the contaminating chain is shorter or longer. For 10 % of a shorter chain the spacing approximates to that of the pure substance, but the number of orders decreases. With a longer contaminating chain the *A* spacing increases steadily up to 80 % impurity. The *A* spacing then is very sensitive to the addition of small amounts of other paraffins. With *n*-hexacosane and *n*-octacosane mixtures, since both have even number chains, we have to deal with two crystal forms. Both crystallise normally in the *C* form but if more than 2·5 % of the longer chain is added to the shorter, crystallisation occurs only in the *A* form. Up to 10 % of a short chain can be added to a long

Table II. *Melting-points and crystal spacings of mixed paraffins.*

($C_{28}H_{58}$ and $C_{29}H_{60}$.)

Percentage composition		Transition-point on heating	M.P.	S.P.	Transition-point on cooling	X-ray analysis			Remarks
							Spacing in Å.		
$C_{28}H_{58}$	$C_{29}H_{60}$					Series number	*A*	*C*	
100	0	57·2–57·4°	61·3–61·5°	61·1°	53·7°	C 114	37	33·25	The *C* form vanishes at contamination 2·5 %
99	1	56·2°	61·2–61·5°	61·1°	53·2°	B 63	—	33·25	
97·5	2·5	56·0°	61·2–61·5°	61·1°	53·4°	B 64	—	33·3	
95	5	56·0°	61·3–61·5°	61·1°	53·6°	B 65	37·55	—	
90	10	55·2°	61·5–61·7°	61·3°	54·2°	B 93	37·8	—	
80	20	55·0°	61·9–62°	61·5°	53·6°	B 92	38	—	
70	30	55·0°	62·1–62·2°	61·7°	53·5°	B 91	37·85	—	
60	40	55·2°	62·3–62·4°	62·0°	53·8°	B 90	38·1	—	
50	50	55·6°	62·3–62·6°	62·3°	54·0°	B 89	38·5	—	
40	60	55·6°	62·6–62·8°	62·4°	54·2°	B 88	38·45	—	
30	70	56·2°	62·8–62·9°	62·5°	54·4°	B 87	38·45	—	
20	80	56·2°	63–63·2°	62·8°	54·7°	B 86	38·6	—	
10	90	56·8°	63·2–63·4°	63·0°	55·2°	B 62	38·7	—	
5	95	57·2°	63·2–63·5°	63·1°	55·4°	B 61	38·7	—	
2·5	97·5	57·5°	63·3–63·5°	63·2°	55·6°	B 60	38·9	—	
1	99	57·5°	63·4–63·6°	63·2°	55·8°	B 59	38·8	—	
0	100	57·5°	63·4–63·6°	63·2°	56·0°	C 26	38·68	—	

Table III. *Melting-points and crystal spacings of mixed paraffins.*

($C_{29}H_{60}$ and $C_{31}H_{64}$.)

Percentage composition		Transition-point on heating	M.P.	S.P.	Transition-point on cooling	X-ray analysis		Remarks
$C_{29}H_{60}$	$C_{31}H_{64}$					Series number	Spacing in Å.	
100	0	57·3–57·5°	63·4–63·6°	63·2°	55·8°	C 26	38·68	
99	1	57·2–57·4°	63·4–63·6°	63·2°	55·4°	C 106	39·12	
97·5	2·5	57–57·5°	63·5–63·7°	63·2°	55·4°	C 96	39·25	
95	5	57–57·2°	63·6–63·7°	63·1°	55·3°	C 97	39·15	
90	10	56·5–57°	63·8–64°	63·3°	55·2–55°	C 98	39·45	
85	15	56·0–56·5°	64–64·2°	63·5°	55–54°*	C 101	39·7	
80	20	56·0–56·5°	64·2–64·4°	63·7°	55–54°*	C 102	39·75	
70	30	56·5–57°	64·6–64·7°	64·1°	55–54°*	C 103	40·55	
60	40	56·5–57°	64·8–65°	64·4°	55–54°*	C 104	40·9	
50	50	57–57·5°	65·3–65·5°	65°	55·5–55°*	C 111	41·2	
40	60	57·5–58°	65·8–66°	65·5°	56–55°*	C 110	41·2	
30	70	59–59·5°	66·2–66·4°	65·8°	57·5–57°*	C 109	41·45	
20	80	60–60·5°	66·6–66·8°	66°	58·5°*	C 105	41·5	
10	90	61–61·5°	67·1–67·3°	66·8°	59·5°	C 108	41·7	
5	95	61·7–61·9°	67·3–67·5°	67·1°	60°	C 100	41·85	
2·5	97·5	61·7–61·9°	67·4–67·6°	67·3°	61·6°	C 99	41·8	
1	99	62·1–62·3°	67·6–67·7°	67·3°	61·7°	C 107	42·0	This increase in spacing is greater than the possible experimental error
0	100	62·3–62·5°	67·6–67·8°	67·3°	61·8°	C 32	41·55	

* = indefinite.

one before the *C* modification fails to appear. This is clearly shown in Plate VIII, Fig. 1. The tables show that this is a true generalisation whether the contaminating paraffin has an odd or an even number chain. There is no measurable change in *C* spacing until the *A* form appears, spacing variations then follow the course described for two odd number paraffins.

Table IV. *Melting-points and crystal spacings of mixed paraffins.*

($C_{26}H_{54}$ and $C_{28}H_{58}$.)

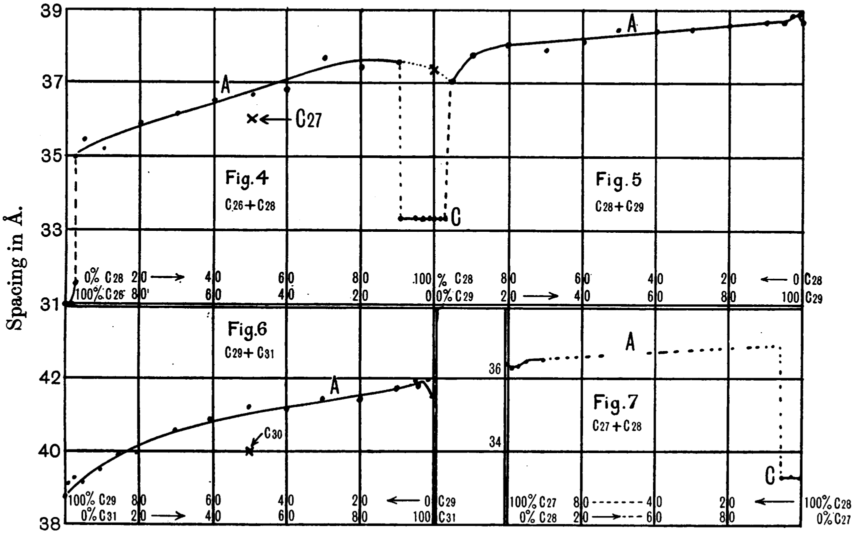
Percentage composition						X-ray analysis			
							Spacing in Å.		
$C_{26}H_{54}$	$C_{28}H_{58}$	Transition-point on heating	M.P.	S.P.	Transition-point on cooling	Series number	*A*	*C*	Remarks
100	0	51·5–52°	56·4–56·6°	56·1°	48·3°	C 67	34·95	31	*C* spacing disappears at more than 2·5 % impurity
99	1	51°	56·5–56·6°	56·0°	48·0°	B 39	—	31	
97·5	2·5	51°	56·5–56·7°	56·0°	47·4°	B 40	35·1	31·6	
95	5	50°	56·5–56·8°	56·0°	47·0°	B 41	35·5	—	
90	10	48·5–49·5°	56·7–57·0°	56·3°	46·5°*	B 42	35·25	—	
80	20	48·5–49·5°	57·2–57·5°	57·0°	46·5°*	B 43	36	—	
70	30	48·5–49·5°	57·8–58°	57·5°	46·5°*	B 44	36·2	—	
60	40	48·5–49·5°	58·4–58·6°	58·2°	47·0°*	B 45	36·55	—	
50	50	49–50°	58·9–59·1°	58·5°	47·4°*	B 97	36·7	—	
40	60	49–50·5°	56·6–56·7°	59·2°	48·8°*	B 46	36·8	—	
30	70	51–52°	60·1–60·2°	60·0°	50·6°*	B 47	37·7	—	
20	80	52–53°	60·4–60·6°	60·1°	52·5°	B 48	37·4	—	
10	90	53–53·4°	61·0–61·1°	60·4°	52·7°	B 49	37·55	33·45	*C* spacing disappears at more than 10 % impurity
5	95	54·5°	61·1–61·3°	60·9°	53·2°	B 50	—	33·35	
2·5	97·5	55–55·5°	61·2–61·4°	60·9°	53·3°	B 51	—	33·3	
1	99	56·5–57°	61·2–61·5°	60·9°	53·4°	B 52	—	33·3	
0	100	57·4°	61·3–61·5°	61·1°	54·0°	C 114	37	33·26	

* =indefinite.

Table V. *Melting-points and crystal spacings of mixed paraffins.*

						Crystal spacing in Å.		
Composition (equimolar unless stated)	Transition-point on heating	M.P.	S.P.	Transition-point on cooling	Series number	*A*	*C*	Remarks
97·5 % C_{26} + 2·5 % C_{27}	49·4–49·6°	56·4–56·6°	56·1°	48°	B 100	—	30·9	
97·5 % C_{27} + 2·5 % C_{26}	52·5–53°	59·0–59·1°	58·6°	—	B 99	36·15	—	
99 % C_{27} + 1 % C_{28}	52·5–53°	59·0–59·1°	58·7°	50·6°	B 55	36·3	—	
97·5 % C_{27} + 2·5 % C_{28}	52·5–53°	59·0–59·2°	58·8°	—	B 56	36·3	—	
95 % C_{27} + 5 % C_{28}	52·5–53°	59·1–59·3°	58·9°	50°	B 57	36·45	—	
90 % C_{27} + 10 % C_{28}	52·5–53°	59·2–59·5°	58·9°	50°	B 58	36·55	—	
99 % C_{28} + 1 % C_{27}	56·8°	61·2–61·4°	61·1°	53·4°	B 66	—	33·2	
97·5 % C_{28} + 2·5 % C_{27}	56·4°	61·2–61·4°	61·0°	53·3°	B 67	—	33·3	
95 % C_{28} + 5 % C_{27}	55·6°	61·2–61·4°	61·0°	53·2°	B 68	—	33·2	
90 % C_{28} + 5 % C_{27} + 5 % C_{29}	55·2°	61·3–61·5°	61·2°	—	B 69	37·7	—	
90 % C_{28} + 5 % C_{26} + 5 % C_{30}	54–54·4°	61·3–61·5°	61·2°	—	B 70	38·0	—	
97·5 % C_{32} + 2·5 % C_{31}	64°	69·4–69·6°	68·8°	63·4°	B 98	—	42·5	
C_{27} + C_{28} + C_{29}	53·4°	61·0–61·4°	60·8°	—	B 54	38·25	—	
C_{26} + C_{28} + C_{30}	50–51°	61·6–61·8°	61·3°	—	B 71	—	—	
C_{26} + C_{27} + C_{28} + C_{29} + C_{30}	44°	61–61·5°	60·7°	—	B 79	—	—	
C_{27} + C_{29} + C_{31}	52·3°	63·5–63·6°	62·8–63°	—	C 86	40·2 37·75	—	
C_{29} + C_{30} + C_{31}	58–59°	65·6–65·7°	65·4°	—	C 84	40·8	—	
C_{31} + C_{35}	55°	70·7–71·2°	70·3–70·5°	—	C 82/3	46·25 43·0	—	Approximate to the spacings of the constituents
C_{34} + C_{35}	69°	73·6–73·9°	73·3°	—	C 89	46·05	—	

A study of Plate VIII, Fig. 1, reveals marked differences in the intensity decrease with increasing order as the mixtures approach equimolar proportions. Little radiation is reflected beyond the fourth order, and the four orders that do appear stand out much more sharply than in the plates of the more nearly pure materials. To make such a comparison fairly it is of course necessary to take the whole range of photographs under identical conditions. An experienced eye can tell from a glance at a photograph whether or not a given specimen is approaching purity, though in the case of odd number paraffins which have no *C* form, it is easy to overestimate the degree of purity attained.



× =X-ray measurements with mixed paraffins

Figs. 4, 5, 6 and 7.

A few complicated mixtures have been examined, but X-ray data lead to no important generalisations. It will however be observed that in equimolar binary mixtures of chains that differ by 4 or more carbon atoms, distorted crystals of both constituents separate, though in the case of octacosane and dotriacontane a melted layer gave only one spacing. In this connection it may be noted that the *A* spacing of octacosane is 37 and the *C* value of dotriacontane 37·8. The mixed crystal from the melt may consist of tilted 32 and upright 28 molecules though the value found, 40 Å., is high.

The melting- and transition-points of mixtures of paraffins.

The melting-, setting- and transition-temperatures of a comprehensive series of mixed paraffins are given in Tables II–V. It is proposed to summarise here only those observations which will aid an observer in judging the purity of a given sample of a paraffin.

Melting-point. The melting-points of mixtures of two paraffins given in Tables II–IV lie in each case on straight lines, see Fig. 9. There is no depression similar to that observed with the fatty acids, alcohols or ketones, so that (for instance) equimolar $C_{26}H_{54}+C_{28}H_{58}$ melts at the same temperature as $C_{27}H_{56}$ (59·1°) and equimolar $C_{29}H_{60}+C_{31}H_{64}$ (65·6°) the same as $C_{30}H_{62}$ (65·7°). In the case of equimolar mixtures of three paraffins, the melting-points are still quite sharp and correspond with the mean molecular weight. In the case of equimolar mixtures of four or more paraffins the melting-points are indistinct, but are in the region corresponding with the mean molecular weight. To give a concrete example the following paraffins and mixtures all melt at approximately the same temperature (61·4–61·6°): $C_{28}H_{58}$, equimolar $C_{27}H_{56} + C_{29}H_{60}$, $C_{28}H_{58} + 5\ \% \ C_{27}H_{56} + 5\ \% \ C_{29}H_{60}$, $C_{28}H_{58} + 5\ \% \ C_{26}H_{54} + 5\ \% \ C_{30}H_{62}$, equimolar $C_{26}H_{54} + C_{28}H_{58} + C_{30}H_{62}$, equimolar $C_{26}H_{54} + C_{27}H_{56} + C_{28}H_{58} + C_{29}H_{60} + C_{30}H_{62}$. It is obvious from these results that the purity of a paraffin cannot be judged by a comparison of melting-point, or by mixed melting-point with a sample of a paraffin of known purity.

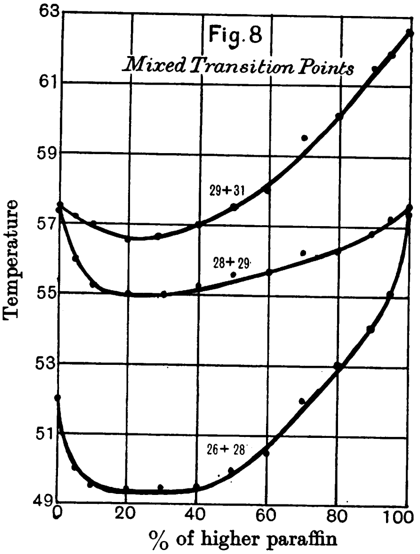


Fig. 8

Mixed Transition Points

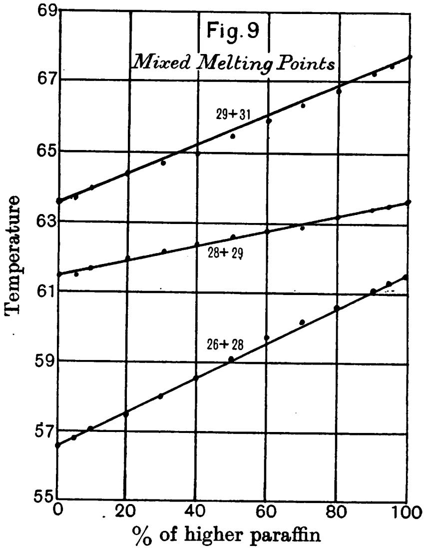


Fig. 9

Mixed Melting Points

Setting-points. In the case of equimolar mixtures of two or three paraffins whose carbon content does not differ by more than two or three carbon atoms, the setting-points are quite sharp and are not appreciably depressed. In the case, however, of a mixture of, say, two paraffins differing by three or more carbon atoms it will be found that the melting-point extends over a somewhat broad range, 0·5–0·7°, and that the upper limit of the setting-point may be higher than the lower limit of the melting-point. This is due to the separation of quite large crystal masses containing an excess of the higher melting constituent. The fact that the setting-point is very close to the melting-point, therefore, is not necessarily a guarantee that the paraffin is pure. Equimolar mixtures containing more than three paraffins do not set crystalline; instead a white dense mist slowly separates from the bottom of the tube upwards.

Transition-points. As we believe that the transition-point alone can serve as a satisfactory guide throughout the separation of a mixture of naturally occurring paraffins, these call for more extended comment. In the case of mixtures of neighbouring paraffins, for example $C_{28}H_{58}$ and $C_{29}H_{60}$ given in Table II, the transition-temperatures on heating and cooling are quite sharp throughout the whole range. If the two paraffins, however, differ by two carbon atoms, then the transition-points on both heating and cooling between the limits of 30 and 70 % of one constituent are not sharp and occur gradually over a range that may be 0·5–1°. In the case of small amounts of impurities, such as 1–5 % of another paraffin, the sharpness of the transition-point is not affected. If however any of these paraffins are melted side by side in the bath with the pure paraffin there is always a recognisable difference in the temperature of transition on heating and especially on cooling.

A careful observation of the transition-point in fact will detect 1 % impurity in a paraffin. It is obvious that the exact temperature at which this transition occurs will depend a little on the rate of heating or cooling of the bath and therefore to make full use of this transition-point it is necessary to have a sample of chemically pure paraffin for comparison.

We have carefully compared the melting-points and transition-points of pure paraffins with those containing other paraffins in the small proportion of 1–5 % as given in Table V. The melting-points of the latter in all cases are raised or lowered according as to whether the admixed paraffin has a longer or shorter chain. When such samples are melted side by side the difference in melting-point is observable though it may be too small to be stated. However, the values obtained for transition-points, especially on cooling, differ appreciably and are never less than 0·2°.

In general our observations suggest that the even number paraffins containing 1–5 % of a neighbouring paraffin show considerably more depression in the transition-point on heating than do the odd number paraffins (Fig. 8).

In the case of approximately equimolar mixtures of two paraffins separated by three or more carbon atoms, the transition-point is not well defined. The contents of the melting-point tube viewed at room temperature show very little crystalline structure. A glassy state is already apparent, and on heating there is no definite first transition. The second transition is however very marked and occurs at 1–1·5° instead of 0·3–0·5° below the melting-point. On cooling the first transition to the glass takes place normally, and this form persists down to room temperature with, perhaps, the appearance of a few cleavages, showing partial reversion to the more usual crystalline form. As will be emphasised later, this marked difference in behaviour is of great practical use.

In the case of equimolar mixtures of three or four paraffins the transition-temperature is very indistinct and occurs at that of the lowest member in the mixture. The transition-point, therefore, can be 10–15° below the actual point of fusion. The one sample of an equimolar mixture of five paraffins that was made, $C_{26}H_{54}$ to $C_{30}H_{62}$ inclusive, showed no appreciable transition-points at all.

GENERAL DISCUSSION.

It will be seen from the experimental data given above that if a paraffin is to be considered pure it must have not only the correct melting-point, but also the correct transition-point. Its spacing will be correct to 0·2 % and the picture will show 8 or more orders. It will also give good microcrystals which display a sharp rhombic cleavage, the angles of which will differ according as to whether the paraffin has an odd or even number of carbon atoms.

In biochemical investigations it is improbable that paraffins of this high degree of purity will be often encountered. Recognising this fact we have, in this research, aimed not only at the establishment of these absolute criteria of purity, but also the collection of evidence which will enable us to suggest the composition of a mixture from which we are unable to separate a chemically pure paraffin. In the following summary we give a number of conclusions which are already aiding us in our investigations of plant waxes. In passing it may be mentioned that mixed paraffins can be readily separated into fractions having different melting-points by means of light petroleum, but that the preparation of a single paraffin of recognisable degree of purity from a mixture is always very laborious, and according to our experience, often impossible.

(1) If a paraffin gives the correct melting-point, and also the correct transition-temperature on both heating and cooling, then it contains less than 1 % of impurity. In such cases confirmation by X-ray analysis is unnecessary.

(2) X-ray analysis alone, without due regard to melting- and transition-points, is insufficient to identify a paraffin. Reference to Table III will show that $C_{31}H_{64}$ and a mixture of 20 % $C_{29}H_{60}$ + 80 % $C_{31}H_{64}$ both have the same spacing (41·5 Å.).

(3) The melting-point curve of a mixture of two paraffins which do not differ by more than 2 carbon atoms is a straight line (Fig. 9). This means that the melting-point of a mixture is determined by its mean molecular weight, and that no depression is exhibited. Within similar limits as to carbon atoms the same is true for mixtures of three paraffins. In respect to melting-point therefore the mixed paraffins are sharply differentiated from the alcohols and acids, which show in most cases very considerable depression. This finding has a very important practical application. In separating the constituent paraffins of a mixture it follows that of any two fractions obtained the one with the higher melting-point will have the higher mean molecular weight. This, of course, is not necessarily so with mixtures of acids or alcohols, in which both the higher and lower acids or alcohols may have melting-points higher than that of the respective mixtures. Francis, Piper and Malkin [1930, p. 227] came to the conclusion that it was extremely difficult, and in some cases impossible, to effect the separation of mixed acids by fractional crystallisation, and it is probable that this also applies to alcohols.

Further we have collected a very large number of observations on the crystallisation of mixed paraffins, and since their layer structure is simpler than those of the acids and alcohols (which contain the length of two molecules between the 001 planes) the interpretation of the X-ray photographs, at this stage, is more straightforward. For this reason we are investigating the composition of the mixed primary alcohols which occur in plant waxes by fractionation of the derived paraffins, in preference to the fractionation of the alcohols themselves or the derived acids as done by previous workers.

(4) It follows from the data given in the above section that a mixture of two paraffins can give the same melting-point as a pure paraffin, but the transition-point will be lower. When such a mixture is melted with this pure paraffin the melting-point will be unchanged, but the transition-point will be either that of the mixture or lower. Therefore an observation confined to the mixed melt—which is the usual laboratory practice—is, by itself, quite insufficient to warrant any conclusion as to purity. The transition-temperature gives this information at once.

(5) If a mixture has a recognisable transition-point, a sharp melting-point, and sets crystalline when the temperature on cooling falls about 0·5°, it is safe to assume that there are not more than three components present in recognisable amounts. If the material melts over an extended range (0·5–1°), and if on cooling crystals come out at a temperature on or above the lower of these limits, then the mixture is probably of two paraffins only whose carbon contents differ by three or more carbon atoms.

(6) The short spacing of an even number paraffin will come up although the sample contains 2·5 % of a longer or up to 10 % of a shorter paraffin. A relatively impure sample of an even number paraffin will therefore show a short spacing which is quite specific and is a positive identification. Unfortunately no such simple means are available for the positive identification of an odd number paraffin of this degree of purity.

(7) In a series of fractions obtained from a mixed paraffin which does not appear to contain more than three components our experience suggests that if the transition-temperatures are some 8–10° below the melting-points, components are even number paraffins, and if 6–8° they are odd. This conclusion must be accepted with caution, as the transition-temperatures are susceptible to very small amounts of impurities.

(8) When attempting to decide upon the constituents of a naturally occurring paraffin in which the maximum degree of separation has been obtained, we first measure the spacing. We are then able to select one or more binary synthetic mixtures which have the same spacing. Of these synthetic mixtures we choose the one in which both the M.P. and transition-point are in best accord with those of the mixture under examination. It is unusual to find a perfect fit, but quite common to find reasonable agreement between the spacings and M.P. Transition-points are considerably depressed by the addition of a small amount of impurity, and it is usual to find the transition-point, when not agreeing with a synthetic mixture of corresponding M.P. and spacing, to be low. In such cases we consider the main constituents of the mixture under

examination to be those of the best agreeing binary mixture with a small (about 5 %) impurity whose constitution we are unable definitely to state. Since we are concerned with establishing the actual presence in bulk of the main constituents rather than in estimation of the exact proportion in which they occur, it is our practice to find the spacings of mixtures which we have not actually prepared from graphs shown to correspond with those of similar mixtures whose spacings have been measured. Thus the spacing curve for $C_{28}H_{58}$ and $C_{30}H_{62}$ is taken to be identical with that for $C_{26}H_{54}$ and $C_{28}H_{58}$, but the scale of ordinates is raised to lie between the appropriate spacings of $C_{28}H_{58}$ and $C_{30}H_{62}$. Similar estimations have been made for transition-points. In each case we have checked this assumption by making one or two appropriate mixtures.

It will be seen from the above recommendations that our experiments, which have been guided throughout by X-ray analysis, bring out quite clearly the importance of the transition-point. In our investigations of plant waxes we are, in fact, now able to dispense entirely with the laborious X-ray analysis in all cases except (*a*) for positive identification, especially with even number paraffins, (*b*) as a guide to the composition of mixtures from which we are unable to obtain fractions of the requisite purity by fractional crystallisation. In the two papers which follow we describe the fractionations of plant waxes which were carried out at the same time as the work described in the present paper. In these cases X-ray analysis was freely used and it will be seen that the final results give, in several instances, practical confirmation of the recommendations given above.

The position of side chains.

Two important papers by Shearer [1925] and Savile and Shearer [1925] have shown how the position of a side-group in a straight chain may be determined by X-rays. We have used this method for identifying ketones and secondary alcohols.

The method may be understood from an inspection of Plate VIII, Fig. 3, which shows the spacings of a series of nonacosanones. All the chain lengths are the same, and the spacings, within 0·25 %, agree with those for nonacosane. The intensities of the lines vary in a marked manner, displaying a periodic intensity variation superimposed on the normal decrease with increasing order. A group at $\frac{1}{3}$ of the chain length gives weak 3rd, 6th, 9th, *etc.*, orders; half-way along the chain it causes the even orders 2, 4, 6, *etc.*, to be very faint. We find that the secondary alcohols have intensity fluctuations of an identical nature, but that the spacings are very much shorter, showing that the molecule is inclined. Also they have both a high and a low temperature form. The spacings give the chain length, and the intensity fluctuations decide the position of the group within about 2 carbon atoms. It must be added that Shearer has pointed out that when the side group is on the last or the penultimate carbon atom the

Table VI. *Melting-points and crystal spacings of ketones and secondary alcohols.*

Abbreviated formula of compound	M.P.	Series number	Crystal spacing in Å.		Remarks
$C_{14}-CO-C_{14}$	80·8°	C 1	38·65		The constant spacing but variable intensity distribution are shown in Plate VIII, Fig. 3
$C_{13}-CO-C_{15}$	74·7°	C 47	38·9		
$C_{11}-CO-C_{17}$	74·7°	C 48	38·9		
$C_{9}-CO-C_{19}$	75·0°	C 49	38·9		
$C_{8}-CO-C_{20}$	74·4°	—	38·8		
			High temp.	Low temp.	
$C_{11}-CHOH-C_{11}$	75·2°	C 6	—	31·5	
$C_{13}-CHOH-C_{13}$	80·5°	—	34·75	36·6	
$C_{14}-CHOH-C_{14}$	84·0°	—	—	37·15	Spacing lower than for the corresponding ketone
$C_{13}-CHOH-C_{15}$	79·5°	—	—	—	Spacing not observed
$C_{11}-CHOH-C_{17}$	74·7°	—	—	36·9	
$C_{9}-CHOH-C_{19}$	75·0°	—	—	—	
d-$C_{9}-CHOH-C_{19}$	82·2°	C 75	—	38·65	Note the high value of this spacing. It corresponds to the *A* spacing of *n*-nonacosane
$C_{8}-CHOH-C_{20}$	75·8°	C 55	—	37·15	
$C_{15}-CHOH-C_{15}$	84·7°	—	39·4	41·25	

Table VII. *Melting-points and crystal spacings of primary alcohols.* Malkin [1930].

Number of C atoms	M.P. (Malkin)	M.P. (A.C.C.)	Crystal spacing in Å. High temperature	Crystal spacing in Å. Low temperature
16	49·0°	—	44·9	37·4
18	59·0°	—	50·2	41·35
19	62·0°	—	52·8	—
20	—	65–65·5°	—	46·2
21	68·5°	—	56·9	57·4
22	72·0°	—	—	49·95
24	76·5–77°	75·6–76°	—	54·0
25	78·5°	77·7–78°	—	68·5

The spacing and M.P. of normal eicosanol are new measurements.

spacing is doubled, owing to crystallisation occurring with 2 carbon chains between the 001 planes like end to like end.

The melting-points and crystal spacings of the secondary alcohols and ketones which appear to us of biochemical importance are given in Table VI. Equimolar mixtures in all cases show a depression of many degrees. We have to thank Dr Malkin for permission to reproduce his data for the higher primary alcohols given in Table VII.

SUMMARY.

Highly pure paraffins from $C_{26}H_{54}$ to $C_{36}H_{74}$ and certain long-chain ketones and secondary alcohols of possible biochemical importance have been synthesised and their crystal spacings determined.

If the melting-point of a pure paraffin is determined in the way described it is possible to determine accurately two transition-temperatures at which a visible change of structure occurs. The lowest of these is markedly affected by impurities and is shown to be of great practical importance.

The melting-points, transition-points and crystal spacings of a comprehensive series of mixed paraffins have been determined.

From the data thus obtained it has been possible to draw up a series of recommendations which will aid in the fractionation and identification of the mixed paraffins which occur in nature, or which can be obtained from the mixed primary alcohols which occur in nature.

Brief reference is made to the work of Shearer [1925] showing how the position of a side group in a straight chain can be determined by X-rays.

In conclusion we should like to thank Prof. Garner and Dr Malkin for supplying us with samples of highly pure paraffins and alcohols, and the Imperial Chemical Industries, Ltd., for a grant towards the expenses of this research.

REFERENCES.

Backmann and Clark (1927). *J. Amer. Chem. Soc.* **49**, 2089.
Brooks (1922). The non-benzenoid hydrocarbons. (New York.)
Channon and Chibnall (1929). *Biochem. J.* **23**, 168.
Drew and Porter (1928). *J. Soc. Chem. Ind.* **47**, 17.
Francis, Piper and Malkin (1930). *Proc. Roy. Soc. Lond.* A **128**, 214.
Garner, van Bibber and King (1931). *J. Chem. Soc.* 1533.
Gascard (1921). *Ann. Chim.* (9), **15**, 332.
Gluud (1919). *Ber. deutsch. chem. Ges.* **52**, 1051.
Grün, Ulbrich and Krczil (1926). *Z. angew. Chem.* **39**, 421.
Hildebrand and Wachter (1929). *J. Amer. Chem. Soc.* **51**, 2487.
Kraft (1882). *Ber. deutsch. chem. Ges.* **15**, 1714.
Levene, West and Van der Scheer (1915). *J. Biol. Chem.* **20**, 521.
Malkin (1930). *J. Amer. Chem. Soc.* **52**, 3739.
Müller and Savile (1925). *J. Chem. Soc.* **127**, 602.
—— —— (1928). *Proc. Roy. Soc. Lond.* A **120**, 437.
—— —— (1930). *Proc. Roy. Soc. Lond.* A **127**, 417.
Peterson (1906). *Z. Electrochem.* **12**, 141.
Piper, Brown and Dyment (1925). *J. Chem. Soc.* **127**, 2194.
—— Malkin and Austin (1926). *J. Chem. Soc.* 2310.
—— and Malkin (1930). *Nature*, **126**, 278.
Pregl (1924). Quantitative organic analysis. Trans. Fyleman. (London.)
Robinson and Robinson (1925). *J. Chem. Soc.* **127**, 2194.
Savile and Shearer (1925). *J. Chem. Soc.* **127**, 592.
Shearer (1925). *Proc. Roy. Soc. Lond.* A **108**, 655.