PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XLIII.—*Oenanthylic Acid and Normal Heptyl Alcohol.*

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Oenanthylic acid, $C_7H_{14}O_2$, was discovered in 1841 by Tilley (*Ann. Chem. Pharm.*, xxxix, 160). He obtained it by oxidising castor-oil with nitric acid and distilling the product with water. A similar acid, called *azoleic acid*, had already been found by Laurent in 1837 among the products formed by the action of nitric acid on stearic acid. Tilley thinks that these two acids were probably identical.

Oenanthylic acid was afterwards examined by Bussy, who found that its aldehyde, or *oenanthol*, was produced by the dry distillation of castor-oil. He obtained the acid by oxidising this compound with nitric acid and with chromic acid (*Ann. Chem. Pharm.*, lx, 246). Williamson showed that the same acid is produced by the action of caustic potash on *oenanthol* (*Ann. Chem. Pharm.*, lxi, 38); and Tilley, who examined *oenanthol* more carefully than Bussy had done, also prepared it by these different methods (*Phil. Mag.* [3], xxxiii, 81, and *Ann. Chem. Pharm.*, lxvii, 103).

Redtenbacher observed *oenanthylic acid* among the products obtained by oxidising oleic acid with nitric acid (*Ann. Chem. Pharm.*, lix, 41), and Schneider obtained it by acting with nitric acid on the products of the dry distillation of rape-oil (*Ann. Chem. Pharm.*, lxx, 107). Arzbaeher found that it is also formed when castor-oil is oxidised with potassium dichromate and dilute sulphuric acid.

Tilley describes *oenanthylic acid* as a colourless limpid liquid, possessing an aromatic odour. After being dried over glacial phosphoric acid, it begins to boil at 148° , but when kept at this temperature for a long time it suddenly blackens and undergoes decomposition. This undoubtedly shows that Tilley's acid was a very impure compound, for a fatty acid containing seven atoms of carbon must boil without decomposition above 200° ; moreover, he found 0.7 per cent. too much carbon.

In Strecker's "Lehrbuch" it is said that this acid boils at 212° , and the same boiling point is found in Gmelin's and most other hand-books. On whose authority this number is given we are unable to state; it appears not improbable that it was calculated according to Kopp's law.

Staedeler says (*J. pr. Chem.*, lxxii, 240) that the acid obtained by

the spontaneous oxidation of oenanthol boiled under a pressure of 725.9 mm. at 118°, and not at 112° as generally stated. These numbers are obviously misprints for 218° and 212°, as has already been pointed out in the *Jahresbericht* for 1857.

Landolt, who prepared this acid by Tilley's original method, found that the product began to boil at 208°, and that half of it distilled constantly between 218.5° and 220° under a pressure of 756.5 mm., and left a black residue (*Pogg. Ann.*, cxvii, 379).

One of us, by oxidising the alcohols obtained from normal heptane, obtained an acid having the composition of oenanthylic acid, and boiling at 219°—222°. As it appeared probable that this acid might be identical with oenanthylic acid, some of the latter was prepared and found to boil under the same conditions at 219°—221°.* On treating equal quantities of the two acids with water and barium carbonate, and evaporating the two solutions to exactly the same volume, thin iridescent plates appeared on cooling, which grew into large plates and broad needles; both salts are anhydrous. From this it was concluded that the two acids are identical (*Phil. Trans.*, clxii, 121).

Since that time Franchimont has obtained by synthesis an acid having the same composition. He converted the hexyl alcohol from Heracleum oil into the nitrile, and decomposed it with caustic potash. The *heptylic acid* thus formed is an oily liquid, boiling under a pressure of 762.7 mm. at 223°—224°, the whole column of the mercury being in the vapour (*Ann. Chem. Pharm.*, clxv, 237).

Franchimont thinks that this acid is most probably identical with that derived from normal heptane, because Zincke and he found that their hexyl alcohol yielded normal caproic acid by oxidation. But it cannot be identical with Tilley's acid, if the latter was a pure compound. He then adds, "This point assumes a different aspect by Schorlemmer's assertion that oenanthylic acid has the same properties (of which, however, only the boiling point is given) as the acid from heptane. But as Schorlemmer describes no other properties, and as seemingly he has not prepared any derivatives besides the barium salts, such a comparison appears very difficult, and in this case at least too venturesome; although it is possible, and even not improbable, that the two acids are identical. By the oxidation of castor-oil with nitric acid a whole series of acids is produced, according to several statements, and it appears to depend on the strength of the nitric acid, as well as on the temperature and duration of the action, which of the acids is obtained in the largest quantity, and therefore the possibility exists (for Tilley found also caproic acid) that a mixture is produced having the observed boiling point (one has only to remember

* These boiling points are not corrected, but were determined at the same time with the same thermometer.

butyro-acetic acid), and then the similarity of the two barium salts is not sufficient reason for declaring the two acids as identical."

Now in the paper referred to it is not stated at all that the oenanthylic acid used for comparison was prepared by oxidising castor-oil with nitric acid. It is a well-known fact that nitric acid is not the best oxidising agent for preparing pure fatty acids, because it readily acts on them and oxidizes them further. It is true that Brazier and Gossleth, who prepared oenanthylic acid in quantity, found that Tilley's original method gave a better yield than any other (*Quart. Journ. Chem. Soc.*, iii, 210, and *Ann. Chem. Pharm.*, lxxv, 249). But as Bussy had already prepared it by oxidising its aldehyde with chromic acid, this method appears to be the only rational one, and for this reason the acid which was compared with that derived from heptane, was obtained by oxidising pure oenanthol with potassium dichromate and dilute sulphuric acid.

Tilley not only analysed his acid, but also prepared the ethyl-ether and a series of salts. But as his acid was very impure, most of the compounds which he describes were also undoubtedly impure substances. None of the other chemists who worked on oenanthylic acid examined any of the derivatives more minutely, and therefore it appeared necessary to undertake a new research on this acid, the results of which we have the honour to lay before the Society.

Preparation of Oenanthylic Acid.—To obtain this acid in quantity, the following method was found to answer best. Castor-oil is subjected to a rapid dry distillation, and the oenanthol purified by fractional distillation. It is not necessary to use a perfectly pure oenanthol; the portion boiling between 150°—160°, containing still some acrolein and other products, may be employed, as the acid obtained from it can easily be purified.*

300 grams of oenanthol are gradually added to a warm solution consisting of 300 grams of potassium dichromate, 450 grams of sulphuric acid, and 900 grams of water. After the action is over, the flask is connected with a reversed condenser, and the liquid boiled for

* On rectifying a large quantity of oenanthol, we found that the boiling point remained for a very long time perfectly constant at 154°, the whole column of the mercury being immersed in the vapour. According to Tilley it boils at 155°, and according to Staedeler at 151°—152°, the latter observation being probably not corrected. The thermometer used for this determination was one of Geissler's new ones, which Zincke has described (*Ann. Chem. Pharm.*, clxi, 94). These thermometers are very short, having as fixed points the boiling point of water and that of naphthalene, which boils constantly at 217°, according to Geissler. The same thermometer was used for determining the boiling points of the acid and its ethyl-ether. After these experiments were finished, the fundamental points were redetermined, and it was found that, under a pressure of 761.7 mm, water boiled at 100.8°, and pure naphthalene at 218°.

some hours. After cooling, the two layers of liquid are separated, and the lower one, containing some oenanthylic acid in solution, is distilled, and the distillate saturated with soda. The upper layer is well shaken with caustic soda, to remove chromic oxide, and the solution of the sodium salt evaporated. On adding sulphuric acid to the concentrated liquid, oenanthylic acid separates out as an oily layer, which was washed with water, and dried over phosphorus pentoxide.

The acid thus obtained contains some acrylic acid, and begins therefore to boil a little above 140° ; the boiling point soon rises to 200° , and then more slowly to 230° ; at the same time the liquid blackens, and a dark residue is left in the flask. On rectifying the higher-boiling portions, it again leaves a dark residue, and water is formed; the distillates must therefore be dried over phosphorus pentoxide, and the fractional distillation continued, until the acid has a constant boiling point, does not act any longer on phosphorus pentoxide, and volatilises without leaving a residue.

Oenanthylic Acid and Oenanthylates.—Pure oenanthylic acid is a limpid, oily liquid, boiling under a pressure of 763 mm. at 223° – 224° . The cold acid has a faint smell, like that of tallow, but on heating it becomes unpleasantly sour and pungent. In a freezing mixture it soon solidifies to plates, or large broad needles. To determine the melting point a quantity of the acid was placed in a wide test-tube of thin glass, and a delicate thermometer, having a correct zero-point, was placed in the centre of the liquid. At -10° the first crystals appeared, and at -11° the whole was a solid mass. The tube was now removed from the mixture of ice and salt; at -10.5° the crystals began to liquefy, and at -10° every crystal had disappeared. Oenanthylic acid, therefore melts and solidifies at -10.5° .

Franchimont's heptylic acid melts at -8° , but he adds that from repeated experiments it appeared that the melting point was probably 2° lower.

The acid obtained from heptane does not solidify in a freezing mixture. This is, however, no proof against its identity with oenanthylic acid, for it is well known that the melting point of a fatty acid is much lowered by an admixture of other acids. Now the heptane from which the acid was obtained had to be separated by fractional distillation from an isomeride boiling only 7° lower, and from an octane boiling about 17° higher, and therefore certainly contained some of these hydrocarbons: consequently the acid also would contain acids corresponding with the hydrocarbons.

The specific gravity of oenanthylic acid, compared with water at 4° , was found to be—

At	0°	=	0.9345
„	8.5°	=	0.9278
„	16°	=	0.9208
„	29°	=	0.9110

Staedler found it at 24° = 0.9167

Landolt „ „ 18° = 0.9179

„ „ „ 20° = 0.9175

The acid from heptane gave the following results:—

At	0°	=	0.9359
„	9°	=	0.9388
„	28°	=	0.9235

Heptylic acid has at 24° the specific gravity, 0.9212.

The analysis of the acid gave the following results:—

0.2426 gave 0.5744 CO₂ and 0.2300 H₂O.

	Calculated.		Found.
C ₇	84	64.61	64.57
H ₁₄	14	10.77	10.53
O ₂	32	24.62	—
	<hr/> 130	<hr/> 100.00	

Ethyl Oenanthylate, C₇H₁₃(C₂H₅)O₂, was prepared by mixing equal volumes of oenanthylic acid and absolute alcohol with half a volume of concentrated sulphuric acid, and heating the mixture for some hours on a water-bath. The ether which separated as a light colourless layer was washed with water and very dilute soda-solution, dried over calcium chloride, and finally over some phosphorus pentoxide. After being purified by fractional distillation, it was obtained as a limpid and very refractive liquid, possessing a fragrant, fruity smell, and boiling under a pressure of 763 mm. at 187°—188°, the whole mercurial column being immersed in the vapour.

0.1936 gave 0.4848 CO₂, and 0.1977 H₂O.

	Calculated.		Found.
C ₉	108	68.35	68.29
H ₁₈	18	11.39	11.34
O ₂	32	20.26	—
	<hr/> 158	<hr/> 100.00	

It has at 16° the specific gravity 0.8735, and does not solidify at -20°, whilst Tilley's ether, which was not purified by fractional distillation, solidified in a freezing mixture.

Ethyl heptylate boils at the same temperature, and has at 24° the specific gravity 0.874; it also does not solidify at -18° .

Potassium Oenanthylate was obtained by allowing its aqueous solution to evaporate at the common temperature, as a transparent jelly; Tilley's salt has the same properties.

Sodium Oenanthylate crystallises in slender ramified needles, when a warm solution is cooled down slowly, whilst on cooling a concentrated down quickly, it solidifies to a gelatinous mass, in which, however, under the microscope, distinct needles can be seen.

Sodium heptylate possesses very similar properties.

Barium Oenanthylate, $(C_7H_{13}O_2)_2Ba$, was prepared by boiling the acid with water and pure barium carbonate; it crystallises from a hot concentrated solution in very thin, small plates, and from a more dilute solution it separates first in little iridescent plates, which soon grow into large plates or flat needles. On evaporating the mother-liquor over sulphuric acid, it crystallised in long needles grouped in stars. This salt has already been described and analysed by several observers.

0.1767 gave 0.0877 $BaCO_3$.

	Calculated.	Found.
Ba	34.68 per cent.	34.51

To determine its solubility, an excess of the salt was added to water contained in a stoppered bottle, and the mixture frequently shaken and kept for several weeks in a cellar having a constant temperature. As most oenanthylates form basic salts on evaporating their solution, the barium was determined as carbonate.

10 c.c. of the solution saturated at 12° gave 0.0848 $BaCO_3$. 100 c.c. contain therefore 1.700 grams of barium oenanthylate.

The barium salt of the acid from heptane has very similar properties; its solubility was determined at the same time.

10 c.c. of the solution saturated at 12° gave 0.0885 $BaCO_3$, or 100 c.c. contain 1.774 grams of the dry salt.

Franchimont did not determine the solubility of barium heptylate, which also crystallises in anhydrous thin plates.

Calcium Oenanthylate, $(C_7H_{13}O_2)_2Ca + H_2O$, was prepared by precipitating a solution of the sodium salt with calcium chloride, and crystallising the washed precipitate from boiling water. It forms very thin, flat, fascicular needles, which dry up to a silky mass.

0.2690 lost at 180° , 0.0160 H_2O .

0.2530 of the dried salt gave 0.0490 CaO .

	Calculated.	Found.
H_2O	5.70	5.94
Ca.	13.42	13.83

OENANTHYLIC ACID AND NORMAL HEPTYL ALCOHOL. 1079

The acid from heptane yields a very similar salt, having the same composition.

0.0632 lost at 180° , 0.040 H_2O .

0.0592 of the dried residue gave 0.0108 CaO .

	Found.
H_2O	6.33
Ca	13.03

The solubility of the two salts was determined by leaving an excess of them in contact with water for six weeks, the mixture being kept in a cellar and frequently shaken.

10 c.c. of the solution of calcium oenanthylate saturated at 8.5° gave 0.0170 CaO .

10 c.c. of the solution of the salt from heptane at the same temperature, gave 0.0170 CaO .

The two salts possess therefore the same solubility; 100 c.c. of a solution saturated at 8.5° contain 0.9046 grams of the anhydrous salt, or 0.9593 of the crystallised salt.

Calcium heptylate has the same composition, but its solubility has not been determined by Franchimont.

Zinc Oenanthylate, $(\text{C}_7\text{H}_{13}\text{O}_2)_2\text{Zn}$, was obtained by adding zinc sulphate to a solution of the sodium salt. The dried precipitate was crystallised from absolute alcohol; on cooling the solution quickly, very small needles are obtained, which, when dry, form silky scales, feeling soft, like powdered talc. When the solution cools down slowly, the salt crystallises in short four-sided prisms. The salt contains neither alcohol nor water, and may be heated without undergoing any change up to 130° , at which temperature it melts, and above this temperature it begins to decompose.

0.1527 of the needles lost at 100° only 0.0009

and the residue left on ignition 0.0380 ZnO .

	Calculated.	Found.
Zn	20.17	20.10

Franchimont's zinc heptylate crystallises also in short prisms, which, however, contain two molecules of alcohol; the dried salt melts at 131° — 132° . As we once obtained our salt in larger prisms, we dried some quickly between filter-paper, and heated a weighed quantity first to 83° , and then to 100° ; but no loss of weight took place, showing that it did not contain alcohol.

Lead Oenanthylate, $(\text{C}_7\text{H}_{13}\text{O}_2)_2\text{Pb}$, was obtained by adding lead acetate to a solution of the sodium salt, as a heavy precipitate, which is not very freely soluble in boiling water, but may be crystallised from it, and is thus obtained in thin, small, iridescent, rhombic plates, or flat needles grouped in stars.

0·2875 of the crystallised salt dried at 125° lost 0·002, and the residue gave 0·1370 PbO.

	Calculated.	Found.
Pb.....	44·51	44·23

Lead heptylate is a similar salt; the precipitated compound melts, according to Franchimont, at 79°—80°. We found that our lead salt only softens at this temperature, and becomes perfectly liquid and transparent only at 90°. The crystallised salt begins to soften at 88°, and liquefies completely at 94°—96°; it solidifies again at 75°—76°.

Tilley describes lead oenanthyate as a lemon-yellow powder, insoluble in water; it appears very probable that this salt owes its colour to a nitro-compound which was present in Tilley's acid.

Copper Oenanthyate, $(C_7H_{13}O_2)_2Cu$, falls down as a soft mass, on adding copper sulphate to a solution of the sodium salt, but on standing the precipitate becomes granular. It is quite insoluble in boiling water, but dissolves readily in absolute alcohol, and is obtained by spontaneous evaporation in green silky needles, or short prisms.

0·2055 gave 0·0501 CuO.

	Calculated.	Found.
Ca.....	19·75	19·47

The copper salt of the acid from heptane, and copper heptylate, are similar precipitates. The former could not, however, be obtained in crystals, but separated from the alcoholic solution as a liquid, drying up to an amorphous mass. Copper heptylate also is first obtained in drops, which afterwards solidify to groups of short prisms.

We prepared our copper salt several times, but it never separated from an alcoholic solution in the liquid state, the solution yielding distinct crystals to the last drop. Tilley also obtained a copper salt, crystallising in green silky needles.

Silver Oenanthyate, $C_{14}H_{13}O_2Ag$, is a white precipitate, crystallising from boiling water, in which it is but sparingly soluble, in small, woolly needles.

0·2150 gave 0·0981 Ag.

	Calculated.	Found.
Ag.....	45·57	45·63

The quantity of the acid from heptane was too small to admit of a more minute study, but as the barium salt and calcium salt have the same composition and solubility as the corresponding oenanthyates, we believe that these two acids are identical.

Heptylic acid also bears the greatest resemblance to oenanthylic acid; only the copper and zinc salts exhibit slight differences. Whether these are essential or not, can only be decided by preparing the salts

under exactly the same conditions, and comparing them directly with each other.

There can be no doubt that oenanthylic acid and heptylic acid are both normal compounds; this, however, does not imply that they are really identical. It is not only possible, but even very probable, that the hexyl alcohol from heracleum-oil, as well as the heptylic acid obtained from it, are optically active, while oenanthylic acid probably does not possess this property.

Normal Primary Heptyl Alcohol, $C_7H_{16}O$.—As by distilling castor-oil any required quantity of oenanthaldehyde may be obtained, this compound appears to be the best starting point for the preparation of the hitherto almost unknown normal heptyl compounds.

Some years ago Bouis and Carlet found that by acting with zinc and acetic acid on oenanthol under pressure, a heptyl acetate is formed, boiling at 181° , and yielding a heptyl alcohol boiling at 165° (*Ann. Chem. Pharm.*, cxxiv, 352).

If these statements be correct, this alcohol cannot be a normal compound, for its boiling point is only 8° higher than that of normal hexyl alcohol. One of us, on repeating these experiments, did not, however, succeed in obtaining a heptyl alcohol, the chief product of the reaction consisting in high-boiling condensation-products of oenanthol (*Ann. Chem. Pharm.*, cxxxvi, 261).

To convert oenanthol into the alcohol, we have therefore made use of the excellent method which Lieben and Rossi have employed so successfully for the reduction of other aldehydes.

Oenanthol was shaken with fifty times its weight of water; and a little more than the required quantity of an amalgam containing 1 per cent. of sodium was gradually added, together with an equivalent quantity of dilute sulphuric acid, care being taken to keep the liquid always slightly acid. As soon as the action was over, the liquid was distilled, and the distillate again treated in the same way with the amalgam. The alcohol floating on the top was then removed, and the portion remaining in the aqueous solution isolated by repeated distillation, the alcohol always coming over with the first portion, from which it was finally separated by adding potassium carbonate. The product was dried over ignited potassium carbonate, and the alcohol separated from another very high-boiling liquid by fractional distillation. To get rid of some oenanthol and water which were still present, the liquid was several times distilled over small pieces of sodium, and then left for several weeks in contact with anhydrous baryta.

Normal heptyl alcohol is a limpid oily liquid, possessing an aromatic odour, and boiling under a pressure of 766 mm. at 175.5° — 177.5° , the whole column of mercury being surrounded by the vapour.

0.2800 gave 0.7405 CO_2 and 0.3483 H_2O .

	Calculated.		Found.
C_7	84	72.4	72.13
H_{16}	16	13.8	13.81
O.....	16	13.8	—
	<hr/> 116	<hr/> 100.0	

This alcohol, as well as other normal heptyl compounds, will be fully described in a second communication.

We are now acquainted with the complete series of normal alcohols up to octyl alcohol. The following table shows that the boiling points increase very regularly for each increase of CH_2 . The boiling points which are here given were determined either by the whole column of the thermometer being immersed in the vapour, or, if this was not the case, the required corrections were made:—

Table of Normal Alcohols.

	Boiling-point.	Difference.	Observer.
Ethyl alcohol	78.4°	—	Kopp.
Propyl alcohol	97°—98°	19°	Different observers.
Butyl alcohol	116°	18.5°	Lieben and Rossi.
Pentyl alcohol	137°	21°	Lieben and Rossi.
Hexyl alcohol	157°	20°	Franchimont and Zincke.
Heptyl alcohol	175.5°—177.5°	19.5°	H. G. and C. S.
Octyl alcohol	196°—197°	20°	Renesse.
Mean.....	..	19.6°	