XLVIII.—*Isomeric Fencholenic Acids.*

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That a striking analogy exists between camphor and fenchone in many of their compounds has been previously shown by Wallach (*Annalen*, 1890, **259**, 325 ; 1892, **269**, 332 ; 1894, **284**, 324 ; 1898, **300**, 294), and by Gardner and the author (Trans., 1897, **71**, 173 ; 1898, **73**, 275, 704, 708). One of the characteristic points in common is the behaviour of the oximes of these substances ; unlike most cyclic oximes, they do not regenerate the original ketone on boiling with dilute acids, but, on the contrary, lose water and pass to an unsaturated nitrile, which gives an unsaturated acid on hydrolysis. The unsaturated acid, $C_9H_{15}\cdot COOH$, isomeric with campholenic acid, which Wallach obtained from fenchonoxime, is known as fencholenic acid, and attention was drawn by this chemist to the fact that, whilst two isomerides were known in the case of campholenic acid, only one acid was obtained from fenchone.

On repeating Wallach's work, it was found that, on hydrolysing the nitrile, the product does not consist, as he states, merely of a mixture of the amide, which is difficult to hydrolyse, and of liquid fencholenic acid, but that a third substance is present in the acid portion of the mixture. This is an isomeride of the liquid acid, and, unlike the latter, is readily crystalline.

It seems probable that Wallach's liquid acid was really a mixture of the solid (β-) and the liquid (α-) acids, as the melting point of the amide which he obtained by heating the ammonium salt is far too low for the amide of the liquid acid—a point on which he him-

self comments. Further, the amides, when not mixed with one another, are very easily purified, a fact which suggests that he was dealing with a mixture of the two acids. Any portion of the acid which he obtained by hydrolysing the amide produced in the first operation would be pure and unmixed with the β-acid, as the amide of the latter hydrolyses with as great ease as the former does with difficulty, and would consequently be wholly converted into acid in the first operation.

Wallach's observations on the boiling point of the nitrile also tend to prove that he was working with a mixture ; his specimen boiled at 217—218°, whereas the experimental work in the present paper shows that the pure nitrile of the liquid acid boils at 211—212°, and that of the solid acid at 217—219°. The mixture of the nitriles produced by the action of dilute sulphuric acid on the oxime boils between 214° and 219° ; the greater portion, passing over at 217—218°, yields 50—60 per cent. of the β-acid.

According to Wallach, the salts of fencholenic acid with the alkalis and alkaline earths do not crystallise, and are ill-defined. This is true in the main of the liquid acid, as the calcium and magnesium salts can be obtained crystalline, but only with difficulty ; in the case of the solid acid, however, the salts of the alkaline earths are readily crystallisable, although those of sodium and potassium are not. The failure of salts of the liquid acid to crystallise appears to be due to the action of water, as the calcium salt after boiling with water no longer crystallises but turns into a sticky paste, an effect which does not appear to be due to any chemical change, for when liberated from this salt the acid boils at the same temperature as before.

The solid fencholenic acid is much more stable towards halogen hydrides than the liquid isomeride ; the latter readily combines with hydrogen chloride and hydrogen bromide, forming crystalline compounds, but corresponding compounds from the solid acid have not yet been obtained, and it resists almost entirely the action of hydrogen bromide at 100°. With bromine, the solid acid forms a liquid and a solid compound ; the latter is a monohydrobromide, and owes its origin to the considerable amount of hydrogen bromide given off during the absorption of the bromine, but whether it is produced by elimination of hydrogen bromide from the dibromide at first formed, or by direct addition of hydrogen bromide, is not clear, although the former seems more probable.

Fenchone consequently corresponds exactly to camphor in giving an oxime which does not regenerate the original ketone by the action of dilute acids, but, losing a molecule of water in two different ways, produces two isomeric unsaturated acids corresponding to α- and β-campholenic acids. The liquid fencholenic acid I have designated as the

α- and the solid as the β-acid, in order to correspond to the liquid and solid campholenic acids.

It may be mentioned that no interconversion between the α- and β-acids, such as is found in the campholenic series, has been observed in the case of the fencholenic acids.

The preparation of fencholenic acid was undertaken with the object of studying its oxidation products to see in what way they agreed with the interesting series of compounds obtained from the two campholenic and pinonic acids. This work is at present under investigation.

EXPERIMENTAL.

Fenchonoxime was prepared from fenchone ($[a]_D + 61\cdot9°$) by Rimini's method (*Gazzetta*, 1896, **26**, ii, 502), for, although this method is somewhat extravagant in the amount of hydroxylamine required, the yield is quantitative, whereas the product obtained by Wallach's method invariably contains some unchanged fenchone, and the yield rarely exceeds 70 per cent. of the theoretical.

The conversion of oxime to nitrile was effected as follows. Fenchonoxime (50 grams) is added to a mixture of 250 c.c. water and 10 c.c. sulphuric acid; on warming, it partially dissolves, but after boiling, separates as a liquid layer on the surface of the water. The boiling is continued for an hour, the contents of the flask are then cooled, the upper layer separated, and the liquid extracted with ether; the nitrile present in the upper layer and in the ethereal extract is then distilled. It boils at 214—219°, and not at 217—218° as Wallach states.

β-Fencholenic Acid.

The nitrile is hydrolysed by heating with alcoholic potash as described by Wallach (*Annalen*, 1892, **269**, 332). After heating for 7 days, the alcohol is removed by distillation in a current of steam, the contents of the distilling flask are diluted with water, and the α-amide, which separates, is filtered off. The aqueous solution is evaporated until two layers separate; the upper layer, consisting of potassium fencholenate, is removed, diluted with water, and thoroughly extracted with ether. On acidification, an oily layer rises to the surface, and after removing this, the liquid is extracted with ether, and the ethereal extract added to the oil previously separated. In the course of 24 hours, crystallisation occurs to a considerable extent, and further crops of crystals are subsequently obtained; when the last crop has been formed by keeping the oil freed from ether at 0° for a long time, there still remains in the oily residue about 10 per cent. of the solid acid, which can only be removed by careful fractionation of the oil in a vacuum, and afterwards placing the portions of higher boiling

point in a freezing mixture. In this way, the liquid acid can be obtained practically pure. Subsequent investigation of the α- and β-nitriles showed that the best separation of the two acids is effected by allowing the hydrolysis to proceed for $2\frac{1}{2}$ instead of 7 days. The whole of the β-nitrile is then converted to acid, whilst only a small quantity of α-acid is formed, owing to the difficulty with which the α-amide is hydrolysed. The α-amide can then be separately used for the preparation of the α-acid. The yield of β-acid by this method is from 55 to 60 per cent., and of α-amide 35 per cent. of the theoretical, the remainder being α-acid.

β-Fencholenic acid may be easily purified by crystallisation from light petroleum; it melts at 72—73°, boils without decomposition at 140·5—141·5° under 12 mm. pressure, and at 259—260° under the ordinary pressure, and has the specific rotatory power $[a]_D + 19·64°$ in alcoholic solution.

0·2200 gave 0·5755 CO_2 and 0·1898 H_2O.   C = 71·41 ; H = 9·58.
$C_9H_{15}·COOH$ requires C = 71·43 ; H = 9·52 per cent.

It is readily soluble in alcohol, ether, ethylic acetate, and acetone; less so in benzene and glacial acetic acid, and crystallises well from these; it is fairly soluble in hot, but only slightly so in cold light petroleum, and crystallises from it in fine, large plates from 2 to 2·5 cm. in length. It immediately decolorises bromine and permanganate solutions, and from its method of formation is undoubtedly unsaturated.

The sodium and potassium salts cannot be obtained crystalline ; on evaporating their solutions, an oil is formed which eventually becomes semi-solid, and similar results are obtained on adding ether to the alcoholic solution of the salts.

The ammonium salt is formed on passing ammonia into a dry ethereal solution of the acid. It is a white powder which is not very stable, losing all its ammonia at 100°, and reproducing fencholenic acid. When heated at higher temperatures in a sealed tube, it gives the corresponding amide.

The salts of the alkaline earths are well defined and crystallise readily, differing in this respect from the corresponding α-salts.

Calcium β-fencholenate, $(C_{10}H_{15}O_2)_2Ca + 3H_2O$, formed by neutralising an alcoholic solution of the acid with lime water, crystallises in small needles which are readily soluble in warm water or alcohol, but only moderately so in the cold.

0·2144 gave 0·0273 H_2O and 0·0275 CaO. H_2O = 12·73 ; Ca = 9·16.
$(C_{10}H_{15}O_2)_2Ca + 3H_2O$ requires H_2O = 12·61 ; Ca = 9·34 per cent.

The barium salt, $(C_{10}H_{15}O_2)_2Ba + 7H_2O$, crystallises in well defined plates, and is less soluble than the calcium salt.

The *magnesium* salt, obtained by adding a fairly concentrated solution of magnesium sulphate to a solution of sodium β-fencholenate, crystallises with $7H_2O$, and is much less soluble than the calcium or barium salts.

The *copper* salt separates in shiny green scales, slightly soluble in water ; on analysis by ignition in hydrogen :

0·3215 gave 0·0513 Cu. Cu = 15·95.

$(C_{10}H_{15}O_2)_2Cu$ requires 15·9 per cent.

The *zinc, ferric, lead*, and *mercuric* salts are precipitated on adding the corresponding chlorides to a neutral solution of the acid.

β-Fencholenamide.—In the very considerable amount of amide formed in the hydrolysis of the nitrile obtained from the oxime, only one substance, that described by Wallach as melting at 113—114°, can be found. The question whether this was the origin of the solid acid was settled by preparing the ammonium salt of the latter and heating it in a sealed tube at 180° for 5 hours ; at this temperature, only a small amount of charring occurred, and on crystallising the contents of the tube from light petroleum and alcohol, the amide melted at 86·5—87·5°. It was readily soluble in ether and alcohol, but in light petroleum it dissolved only slightly when warm, and was practically insoluble when cold ; it crystallised in soft, silky needles.

0·1989 gave 15·32 c.c. nitrogen at 18·5° and 739 mm.   N = 8·59.

$C_9H_{15}\cdot CONH_2$ requires N = 8·38 per cent.

α- and β-Fencholenic Nitriles.

On warming the β-amide with phosphorus pentoxide on the oil-bath at 60°, it passes readily to the corresponding nitrile, which is purified by pouring into water and distilling in steam.   The β-nitrile is a clear, colourless liquid with a specific gravity of 0·9203 at 15·6°, and a specific rotatory power of $[a]_D + 43·66°$ in alcoholic solution ; it boils at 217—219°, and appears at first sight to be identical with Wallach's nitrile (b. p. 217—218°). This, however, is not the case, since both the nitrile and its corresponding amide pass quantitatively and with the greatest ease to β-fencholenic acid on hydrolysis, the time required being only about one-tenth of that necessary for the conversion of the α-amide to its acid.

To compare the α- and β-nitriles, the former was prepared by a similar method to that employed for the latter from the amide melting at 113—114°.   In this case, the action is not so rapid, and a higher temperature being required, a certain amount of decomposition takes place.   The α-nitrile was purified as before, and boiled constantly at 211—212° ; its specific gravity was 0·9136 at 15·6°, and the

specific rotatory power was $[a]_D + 28\cdot98°$ in alcoholic solution.   On boiling with alcoholic potash, this nitrile is readily converted into the amide melting at 113—114°, but only with difficulty into the liquid acid ; 30 grams of nitrile, after 14 days boiling, give 14—15 grams of the latter.

In the production of the two nitriles from the oxime, it was thought that the strength of the acid might be an important factor in the formation of the two acids.   Investigations were consequently made with 4, 8, 16, and 32 per cent. sulphuric acid, but in no case was any marked difference observed.   Variation in the length of time during which the boiling was continued also had no effect on the yield.

Action of Halogens on a- and β-Fencholenic Acids.

Both acids decolorise bromine on the addition of the latter to their solutions in light petroleum, cooled in a freezing mixture. During the action, a considerable amount of hydrogen bromide is evolved in each case.   After evaporation of the petroleum, the solid acid gives a crystalline compound and a thick, black oil ; the former may be easily obtained pure by means of light petroleum, in which it is not very soluble.   It crystallises in long, thin needles, melts at 80—81° without decomposition, and is insoluble in caustic soda solution.   Analysis shows it to be formed by the addition of the elements of hydrogen bromide to fencholenic acid.

0·1921 gave 0·1452 AgBr.   Br = 32·23.
$C_{10}H_{17}O_2Br$ requires Br = 32·13 per cent.

Towards hydrobromic acid, solid fencholenic acid is very stable. Whilst the liquid acid combines with it when left at ordinary temperatures, the solid acid does not form an addition product, either in the cold or on heating in a sealed tube with acetic and hydrobromic acids at 100°, and in the latter case is for the most part recovered unchanged, mixed with a small amount of oil which contains only a very small percentage of bromine.   The hydrobromide of the liquid acid melts at 96—100°, and is difficult to obtain pure, as it decomposes and liquefies in the air.   The hydrochloride melts, as Wallach states, at 97—98°.

a-Fencholenic Acid.

a-Fencholenic acid is obtained pure by hydrolysing the amide melting at 113—114°, and distilling the acid thus produced.   It is a thick, colourless oil boiling at 136—138° under 12 mm. pressure, and at 254—256° under ordinary pressure, with a slight amount of decomposition.   It is heavier than, and insoluble in, water ; the specific

gravity is 1·0069 at 16°, the specific rotatory power is $[a]_D + 30·73$ (not in solution).

0·2168 gave 0·5661 CO_2 and 0·1846 H_2O.   C = 71·21 ; H = 9·46.
$C_9H_{15}\cdot COOH$ requires C = 71·43 ; H = 9·52 per cent.

According to Wallach, the salts of this acid do not crystallise. The *calcium* salt, $(C_{10}H_{15}CO_2)_2Ca + 4H_2O$, however, may be obtained crystalline by neutralising a solution of the acid in alcohol with lime water, and then rapidly evaporating the solution by heating in a vacuum. The crystalline salt was filtered, dried, and analysed, the water being determined at 80°, as decomposition ensues at 100°.

0·3227 gave 0·0512 H_2O and 0·0412 CaO. H_2O = 15·87 ; Ca = 9·11.
$(C_{10}H_{15}CO_2)_2Ca + 4H_2O$ requires H_2O = 16·14 ; Ca = 8·97 per cent.

Prolonged contact with water, or boiling with water, turns the crystalline salt into a gummy mass which resists all attempts at crystallisation.

The *magnesium* salt is obtained in the same way as that of the β-acid, but is very sensitive to the action of water, and cannot be obtained sufficiently well-defined for analysis.