# 51. *The Constituents of Indian Turpentine from* Pinus longifolia, *Roxb. Part III (continued).*

By A. E. Bradfield, E. M. Francis, and J. L. Simonsen.

The formation of longifolic and *iso*longifolic acids (J., 1923, **123**, 2642) by the oxidation of longifolene * suggested the presence of a vinyl side chain in the hydrocarbon. It seemed possible that the formation of longifolic acid might have involved a molecular rearrangement, since one is undoubtedly concerned in the simultaneous formation of the diketone, *d*-longif-1 : 2-dione (*loc. cit.*, p. 2647), and therefore, before further experiments were initiated, it was of importance to establish beyond question the presence of the vinyl group.

The oxidation of longifolene with ozone yielded formaldehyde and an ozonide, which, on digestion with water and treatment with hydrogen peroxide, gave a lævorotatory acid, $C_{14}H_{22}O_2$. This acid was obtained in dimorphic forms, m. p. 140—142° and 121—122° : it is isomeric with longifolic and *iso*longifolic acids, and the name *α-longifolic acid* is proposed for it. There can therefore be no doubt that longifolene contains a vinyl side chain; in only one other case, that of pimaric acid (Ruzicka, de Graaf, Goldberg, and Frank, *Helv. Chim. Acta*, 1932, **15**, 915), has this group been found in a member of the terpene series.

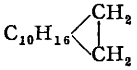
The statement (*loc. cit.*) that *iso*longifolic acid is optically inactive has now been found to be incorrect. The relationship of the three isomeric acids is discussed on p. 191.

In view of the known stability of longifolic acid it was decided to attempt to replace the carboxyl group by an amino-group, from which the corresponding alcohol and hydrocarbon could be prepared. It was anticipated that the latter would prove suitable for degradation. The poor yield of longifolamide obtained from the acid chloride and ammonia in the usual manner (*loc. cit.*, p. 2656) is due to the great ease with which the amide is dehydrated to the nitrile. Under conditions which reduce this secondary reaction to a minimum, longifolamide can be prepared in excellent yield. The conversion of this through the urethane into 1-*amino*-1-*methyllongifane* presented little difficulty and this base was prepared in considerable quantity. Since a mixture of longifolic and *iso*longifolic acids was used in its preparation, the base was a mixture of stereoisomerides. No attempt was made to separate these, but the mixture was characterised by the preparation of a number of crystalline derivatives, some of which were isolated in two forms. Two *methiodides*, α-, m. p. 258—259°, and β-, m. p. 160—162°, were prepared, the hydroxides of which on distillation under diminished pressure lost methyl alcohol with the formation of the dimethylamino-base, isolated as its *hydrochloride* ; only small traces of neutral products were formed simultaneously. Treatment of the base with sodium nitrite in the presence of mineral acid or acetic acid caused much resinification, but a satisfactory yield of a mixture of hydrocarbons and alcohol was obtained when the phosphate of the base was treated with sodium nitrite in the presence of steam.

Although no direct evidence was available, it had been deduced from the general properties of longifolic acid that the carboxyl group was attached to a quaternary carbon atom. This conclusion received confirmation in the fact that the alcohol obtained from the base, although not pure, did not react with phthalic anhydride at 110—120° and was therefore a tertiary alcohol.

Dehydration of the alcohol–hydrocarbon mixture with potassium hydrogen sulphate gave a hydrocarbon, $C_{13}H_{20}$, which, although it had a constant boiling point, consisted of at least three isomerides. Titration with a standard peroxide solution indicated 40% of a saturated tetracyclic hydrocarbon, the presence of which limited severely the material available for degradation. Preliminary experiments showed that the unsaturated hydro-

---

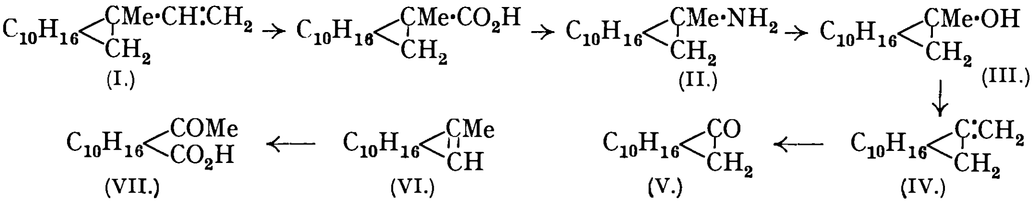
* The tricyclic nucleus  $C_{10}H_{16}\langle\begin{smallmatrix}CH_2\\ |\\ CH_2\end{smallmatrix}$ present in longifolene has been designated *longifane* : the sesquiterpene will then be 1-methyl-1-vinyllongifane, and longifolic acid 1-methyllongifane-1-carboxylic acid.

carbon in the mixture gave formaldehyde on ozonolysis, indicating the presence of a methylene group. Oxidation of the mixture with permanganate in alkaline solution was very slow, but two crystalline products were isolated in extremely small yield: (a) a dibasic *acid* (F), $C_{13}H_{20}O_4$, m. p. 235—236°, which gave a liquid anhydride on digestion with acetyl chloride, and (b) a *lactone*, $C_{12}H_{18}O_2$, m. p. 190°.

The mixture was submitted to ozonolysis, and the ozonides decomposed by catalytic hydrogenation as suggested by Fischer, Düll, and Ertel (*Ber.*, 1932, **65**, 1467). In addition to formaldehyde and the saturated hydrocarbon, a ketone, $C_{12}H_{18}O$, characterised by the *semicarbazone*, m. p. 208—209°, and a mixture of acids were obtained. The quantity of ketone was insufficient for purification, but it was shown to contain a methylene group adjacent to the carbonyl group by the preparation of a liquid hydroxymethylene derivative, from which a crystalline *semicarbazone*, $C_{14}H_{21}O_2N_3$, m. p. 199°, was prepared.

The tetracyclic hydrocarbon, 1-*methyldehydrolongifane*, referred to above was readily obtained pure. Its formation by the dehydration of a tertiary alcohol suggested by analogy that it contained a *cyclo*propane ring, and support was lent to this suggestion by the fact that it gave with hydrogen chloride in ethereal solution a liquid *hydrochloride*, which, although it was not obtained pure, had the composition $C_{13}H_{21}Cl$. The molecular refraction of the hydrocarbon ($[R_L]_D$, 54·11. Calc. for $C_{13}H_{20}$, 53·60) shows an exaltation of 0·51, which is of the same order as that shown by tricyclene (0·80) (Östling, J., 1912, **101**, 472).

If the conversion of 1-amino-1-methyllongifane (II) into the alcohol (III) and the unsaturated hydrocarbon (IV) is unaccompanied by molecular rearrangement, the degradation of longifolene (I) to the ketone longif-1-one (V) can be represented by the scheme:



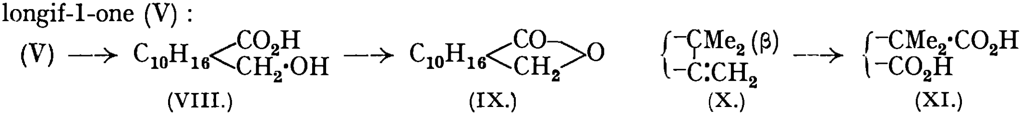
$$C_{10}H_{16}{<}\begin{array}{l}CMe\cdot CH{:}CH_2\\ CH_2\end{array}\ \text{(I.)} \rightarrow C_{10}H_{16}{<}\begin{array}{l}CMe\cdot CO_2H\\ CH_2\end{array} \rightarrow C_{10}H_{16}{<}\begin{array}{l}CMe\cdot NH_2\\ CH_2\end{array}\ \text{(II.)} \rightarrow C_{10}H_{16}{<}\begin{array}{l}CMe\cdot OH\\ CH_2\end{array}\ \text{(III.)}$$

$$\downarrow$$

$$C_{10}H_{16}{<}\begin{array}{l}COMe\\ CO_2H\end{array}\ \text{(VII.)} \longleftarrow C_{10}H_{16}{<}\begin{array}{l}CMe\\ \| \\ CH\end{array}\ \text{(VI.)} \qquad C_{10}H_{16}{<}\begin{array}{l}CO\\ CH_2\end{array}\ \text{(V.)} \longleftarrow C_{10}H_{16}{<}\begin{array}{l}C{:}CH_2\\ CH_2\end{array}\ \text{(IV.)}$$

The mixture of acids obtained after decomposition of the ozonides (above) gave reactions indicating the presence of a carbonyl group. Probably, therefore, the unsaturated hydrocarbon (IV) was mixed with the isomeride (VI), which would give rise to the ketonic acid (VII). However, neither this acid nor the dibasic acid corresponding to it could be obtained pure.

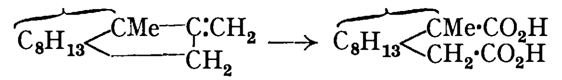
The isolation of the lactone $C_{12}H_{18}O_2$ (IX), m. p. 190°, as a product of the oxidation of the hydrocarbon (IV) with potassium permanganate is in agreement with the suggested structure, since the parent hydroxy-acid (VIII) might result by the degradation of longif-1-one (V):



$$\text{(V)} \longrightarrow C_{10}H_{16}{<}\begin{array}{l}CO_2H\\ CH_2\cdot OH\end{array}\ \text{(VIII.)} \longrightarrow C_{10}H_{16}{<}\begin{array}{l}CO-\\ CH_2\end{array}{>}O\ \text{(IX.)} \qquad \left\{\begin{array}{l}-CMe_2\ (\beta)\\ -C{:}CH_2\end{array}\right.\ \text{(X.)} \longrightarrow \left\{\begin{array}{l}-CMe_2\cdot CO_2H\\ -CO_2H\end{array}\right.\ \text{(XI.)}$$

It is somewhat more difficult to account for the formation of the acid (F) (see above) in the same reaction. An obvious analogy is the formation of camphenecamphoric acid by the oxidation of camphene. The ring widening involved may be connected with the absence of a hydrogen atom attached to the β-carbon atom, as indicated in the partial formulæ (X) and (XI). If one of the β-carbon atoms in the " camphene " hydrocarbon (IV) also has no hydrogen attached to it, the formula for this hydrocarbon may be expanded to (XII) and the dibasic acid (F) represented by (XIII).

(XII.)



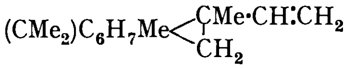
$$C_8H_{13}{<}\begin{array}{l}CMe-C{:}CH_2\\ \quad\ \ \ \ -CH_2\end{array} \longrightarrow C_8H_{13}{<}\begin{array}{l}CMe\cdot CO_2H\\ CH_2\cdot CO_2H\end{array}$$

(XIII.)

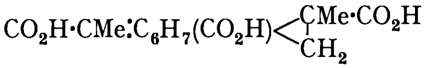
Further insight into the structure of longifolene was obtained by a study of its oxidation with manganese dioxide and sulphuric acid and with nitric acid. With the former it gave trimellitic acid and an acid yielding a crystalline methyl ester, m. p. 145—147°, which was not identified.

The oxidation of longifolene with nitric acid, which was somewhat difficult to control, gave an extremely complex mixture of acids, from which, by the methods detailed on p. 192, the following were separated : a tribasic *acid* (A), $C_{14}H_{18}O_6$, m. p. 283—285°, a tribasic *acid* (B), $C_{15}H_{20}O_6$, m. p. 222—224°, a dibasic *acid* (D), $C_{11}H_{18}O_4$, m. p. 183—185°, *as*-dimethylsuccinic acid, and dimethylmalonic acid. *as*-Dimethylsuccinic acid has been obtained already by the oxidation of longifolic acid with potassium permanganate (*loc. cit.*, p. 2658) and its formation is of importance in establishing the presence of a *gem*-dimethyl group in the hydrocarbon. The tribasic acid (A), which was formed in the largest quantity, is extremely stable and all its carboxyl groups are attached apparently to quaternary carbon atoms, since its acid chloride cannot be brominated and it can only be titrated electrometrically. Its formation from longifolene can be readily explained if its three carboxyl groups are formed by the oxidation of (a) the vinyl group and (b) two methyl groups not attached to the same carbon atom. The methyl group attached to the same carbon atom as the vinyl group cannot be involved, and, since the acid is not a malonic acid, only one of the methyl groups attached to the *gem*-dimethyl group is concerned in its formation. This necessitates the presence in the hydrocarbon of a further methyl group and enables us to expand the formula of longifolene to (XIV) ; the tribasic acid (A) would then be (XV).

(XIV.)



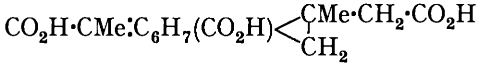
$$(CMe_2)C_6H_7Me{<}\begin{matrix}CMe{\cdot}CH{:}CH_2\\ |\\ CH_2\end{matrix}$$



$$CO_2H{\cdot}CMe{:}C_6H_7(CO_2H){<}\begin{matrix}CMe{\cdot}CO_2H\\ |\\ CH_2\end{matrix}$$

(XV.)

(XVI.)

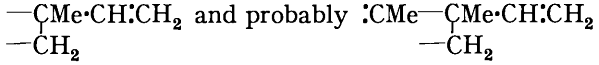


$$CO_2H{\cdot}CMe{:}C_6H_7(CO_2H){<}\begin{matrix}CMe{\cdot}CH_2{\cdot}CO_2H\\ |\\ CH_2\end{matrix}$$

The dibasic acid (D) cannot result from a simple degradation of the longifolene nucleus, since it must be monocyclic and a ring fission is therefore involved in its formation. As the study of its reactions should throw further light on the constitution of the sesquiterpene, it is hoped to prepare this acid in quantity.

The isolation of the acid (B) containing fifteen carbon atoms was unexpected, but its formation is evidently due to the addition, prior to oxidation, of a hydroxyl (or nitro-) group to the α-carbon atom of the vinyl side chain and the acid may be represented by (XVI).

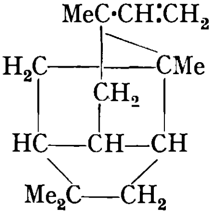
The data available are insufficient to provide rigorous proof of the structure of longifolene, but they limit very considerably the number of possible formulæ if we assume the hydrocarbon to be built up from three isoprene nuclei. Any constitution must accord with the following facts : (i) the ring structure is extremely stable ; it cannot therefore contain a *cyclo*propane ring, and a *cyclo*butane ring is somewhat improbable ; (ii) it must contain a *gem*-dimethyl group as a part of the ring structure ; (iii) it must contain a *cyclo*hexane ring substituted in the 1 : 2 : 4-positions ; and (iv) it must contain the group

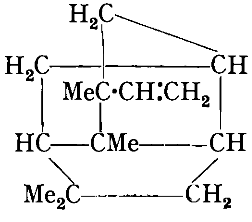


$$\begin{matrix}{-}CMe{\cdot}CH{:}CH_2\\ |\\ {-}CH_2\end{matrix}\ \text{and probably}\ {:}CMe{-}\begin{matrix}CMe{\cdot}CH{:}CH_2\\ |\\ {-}CH_2\end{matrix}$$

Of the possible tricyclic structures containing only *cyclo*pentane and *cyclo*hexane rings which fulfil these conditions, we suggest as the most probable (XVII) and (XVIII). The former is preferred as a representation of longifolene, since it only can give rise to a tetracyclic hydrocarbon structure containing a *cyclo*propane ring. A study of the models of the suggested formulæ for longifolene and the tetracyclic hydrocarbon shows them to be without strain.

(XVII.)



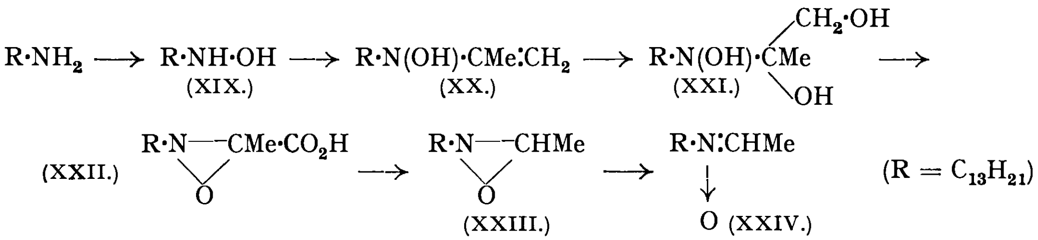


(XVIII.)

There is one fact which appears to be in disagreement with these structures. The dibasic acid (F) (p. 189) obtained by the oxidation of the unsaturated hydrocarbon with potassium permanganate gives an anhydride. On the basis of the suggested formula (XVII) for longifolene this acid would be a substituted adipic acid. A study of the model of this acid has shown that anhydride formation from the *cis*-modification should occur readily, since one of the carboxyl groups is fixed by its position in the dicyclic structure. We do not therefore regard this as a valid objection, more especially since the related Blanc rule has been shown not to hold in polycyclic structures.

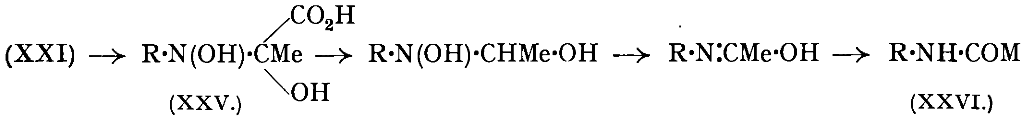
Of the three forms of longifolic acid which have been prepared, two, *iso*longifolic and α-longifolic acids, are optically active; their relationship to one another has not been fully elucidated. These acids contain the structure $>CMe{\cdot}CO_2H$ in which the quaternary carbon atom is asymmetric and there appears to be little doubt that longifolic and *iso*longifolic acids, which are always formed simultaneously, are *cis-trans*-isomerides, as was previously suggested. α-Longifolic acid is possibly a stereoisomeride of either the *cis*- or the *trans*-modification, the isomerism involving optical inversion of one of the other asymmetric centres present in the molecule.

Somewhat remarkable results were obtained by the oxidation of 1-amino-1-methyllongifane with potassium permanganate in acetone solution, an experiment made with the object of effecting ring fission at the $\vdots CMe{\cdot}NH_2$ group. The two main products of the reaction were (i) α-1-*acetamido*-1-*methyllongifane* and (ii) an *acid* (E), $C_{16}H_{25}O_3N$, m. p. 122—124°, which gave by loss of carbon dioxide a *substance*, m. p. 144°, isomeric with α-1-acetamido-1-methyllongifane and from which the base was obtained by digestion with alcoholic sulphuric acid. The formation of these substances can be explained most simply if the hydroxylamine (XIX) is the primary product of the reaction. This would condense with the enolic form of acetone to give (XX), which would be oxidised by permanganate to the trihydroxy-compound (XXI), from which, by loss of water and further oxidation of the primary alcohol group, the acid (E) (XXII) would result. Elimination of carbon dioxide from this would give the isomeride (XXIII) of α-1-acetamido-1-methyllongifane. This is simply an *N*-alkyl derivative of acetaldoxime and may be written (XXIV): its hydrolysis to 1-amino-1-methyllongifane, involving a Beckmann rearrangement, would be anticipated.



(XIX.) (XX.) (XXI.) (XXII.) (XXIII.) (XXIV.)

Whilst the mechanism outlined above explains satisfactorily the formation of the acid (E), it does not account for the formation of α-1-acetamido-1-methyllongifane. It is of course possible that (XXIV) is formed during the course of the reaction, but its isomerisation to the acetyl derivative involves a Beckmann change in an alkaline medium. In our opinion it is more probable that the acetyl derivative (XXVI) owes its formation to the oxidation of (XXI) to the dihydroxy-acid (XXV), from which it would result by the loss of water and carbon dioxide:



$$(XXI) \longrightarrow \underset{(XXV.)}{R{\cdot}N(OH){\cdot}CMe{<}^{CO_2H}_{OH}} \longrightarrow R{\cdot}N(OH){\cdot}CHMe{\cdot}OH \longrightarrow R{\cdot}N{\vdots}CMe{\cdot}OH \longrightarrow \underset{(XXVI.)}{R{\cdot}NH{\cdot}COMe}$$

It is proposed to study the mechanism of this reaction with more readily accessible bases.

## EXPERIMENTAL.

*Oxidation of Longifolene.*—(1) *With ozone.* The hydrocarbon (10 g.) in carbon tetrachloride (20 c.c.) was treated at 0° with ozone until this passed freely through the solution: formaldehyde was detected in the issuing gas. After removal of the solvent under diminished pressure, the ozonide was decomposed with water on the water-bath. The heavy brown oil obtained, consisting of a mixture of an acid and an aldehyde, was kept for 24 hours with an excess of hydrogen peroxide. The crude acid was dissolved in ligroin and shaken with sodium hydroxide, and the alkaline solution, which contained a liquid, sparingly soluble sodium salt, was separated and acidified. The liberated acid, which slowly solidified, was washed with formic acid, dried on porous porcelain, and recrystallised from formic acid, in which it was very sparingly soluble, and then from ligroin (b. p. 40—60°). *α-Longifolic acid* formed soft needles, m. p. 140—142°, $[\alpha]_{5461}$ − 31° (in ethyl alcohol; *c*, 3·86) (Found: C, 76·0; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·7; H, 10·1%). A labile form, m. p. 121—122°, obtained on one occasion, when melted and seeded with the higher-melting modification, resolidified and the m. p. was now 140—142°. In its general properties α-longifolic acid closely resembles its isomerides, although it is more sparingly soluble in the usual solvents. Its methyl ester is an oil.

*iso*Longifolic acid has now been found to have $[\alpha]_{5461}$ − 12·7° (in ethyl alcohol; *c*, 14·064); methyl *iso*longifolate has $[\alpha]_{5461}$ + 5·94° (in methyl alcohol; *c*, 4·68).

(ii) *With manganese dioxide and sulphuric acid.* To a mixture of longifolene (15 g.), water (450 c.c.), and sulphuric acid (375 c.c.) boiling under reflux, manganese dioxide (220 g.) was added gradually. After 18 hours the solution was filtered, unchanged hydrocarbon extracted with ether, and the diluted sulphuric acid solution extracted with ether in a constant extraction apparatus for 24 hours. The dried ethereal extract was evaporated, leaving a gummy solid (2·7 g.). This was dissolved in hot water and the crystals (M) (0·2 g.) which separated on cooling were collected. The filtrate was evaporated, and the residual acid converted through the silver salt into the methyl ester, b. p. 200—210°/13 mm. Hydrolysis of the methyl ester with concentrated hydrochloric acid at 140° gave an acid, which after two crystallisations from hydrochloric acid had m. p. 219—221°, both alone and after admixture with authentic trimellitic acid (Found: C, 51·2; H, 2·9. Calc.: C, 51·4; H, 2·9%). The acid (M), decomp. about 262°, crystallised from dilute methyl alcohol in rosettes of needles, decomp. 264—265° (darkening at 240°). Its *methyl* ester, prepared from the silver salt, crystallised from methyl alcohol in silky needles, m. p. 145—147° [Found: C, 65·3; H, 5·5. $(C_3H_3O)_n$ requires C, 65·5; H, 5·4%]. The acid was not identified.

(iii) *With nitric acid.* To a hot mixture of nitric acid (*d* 1·4; 350 c.c.) and water (500 c.c.), longifolene (100 g.) was added in small quantities: the green oil produced decomposed with evolution of gas and care was necessary to prevent an explosive reaction. The mixture was heated on the water-bath with occasional shaking for 5 days, nitric acid (*d* 1·4; 100 c.c.) being added after the first day. The acid solution from two such oxidations was decanted from a heavy brown oil and concentrated on the water-bath, with occasional addition of water, to a small bulk, a crystalline acid (Y) (11 g.) which separated was collected, the filtrate further concentrated, a second crop (1 g.) of crystals added to (Y), and the filtrate finally evaporated on the water-bath, with occasional addition of water, until quite free from nitric acid, a yellow oil (X) being obtained.

The dry solid (Y) was shaken with chloroform, the insoluble portion extracted with acetone, and the residue (5·4 g.) crystallised repeatedly from formic acid, an *acid* (A) being obtained in rosettes of prismatic needles, decomp. 283—285° (sintering at 258°) or, if rapidly heated, at 289°. The acid crystallised also from methyl alcohol in prismatic needles, which changed in the solvent to massive rhombohedra, decomp. 272—273° (Found: C, 59·2; H, 6·8. $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%). The rotatory power, $[\alpha]_{5461}$ − 36·25°, of the sodium salt was determined in water. The acid (A) was sparingly soluble in water, acetone, and chloroform, more readily in hot acetic acid, formic acid, and methyl alcohol. It was extremely weak and did not give satisfactory results on titration with phenolphthalein as indicator. The molecular weight, kindly determined by Mr. W. C. Evans, B.Sc., by electrometric titration, was 292, calculated as tribasic from the second neutralisation point (calc. from the formula weight, 282). The acid (A) could be recrystallised from concentrated nitric acid and it was not attacked by potassium permanganate in hot alkaline solution or by chromic acid in acetic acid. It was recovered unchanged after fusion with potassium hydroxide or after treatment with hydrogen bromide in acetic acid at 180°. Selenium at 300° had no action on it. The *methyl* ester, prepared from the silver salt by methyl iodide in benzene, crystallised from dilute methyl alcohol in soft prismatic needles, m. p. 73—74°, $[\alpha]_{5461}$ + 42·2° (in ethyl acetate; *c*, 3·556) [Found : C, 62·6; H, 7·7; *M* (Rast), 320·7. $C_{17}H_{24}O_6$ requires C, 62·9; H, 7·4%; *M*, 324].

The acetone extract from the acid (A) was concentrated and, after removal of a further quantity of this acid, evaporated completely; the residual gum (1·3 g.) crystallised when triturated with formic acid. The *acid* (B), after repeated crystallisation from hot water, was obtained in prisms, decomp. 222—224°; $[\alpha]_{5461}$ + 52·81° (in ethyl alcohol; *c*, 2·630) (Found : C, 60·6; H, 7·0. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·7%). It was readily soluble in hot water, alcohol, and acetone, sparingly in cold formic acid and chloroform. When heated with acetyl chloride, it gave a gummy anhydride, insoluble in sodium carbonate but soluble in sodium hydroxide solution. The tribasicity of the acid was determined by Mr. W. C. Evans by electrometric titration (Found : *M*, 302. Calc., 296). Like the acid (A), the acid (B) was extremely resistant to reagents. The methyl ester was an oil.

In one experiment, in place of the acid (B), an isomeric *acid* (C) was obtained, which crystallised from hot water in long prisms, m. p. 199—200° (sintering at 190°) (Found : C, 60·7; H, 7·2. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·7%). On digestion with acetyl chloride it gave a crystalline *anhydride*, which separated from ligroin in long needles, m. p. 103° (Found : C, 64·5; H, 7·0. $C_{15}H_{18}O_5$ requires C, 64·7; H, 6·5%).

The chloroform extract of the original mixture of acids (Y) gave on evaporation of the solvent a gum. This was dissolved in hot water and boiled with an excess of calcium hydroxide, the sparingly soluble calcium salt removed, and the filtrate acidified. The small quantity of acid deposited was crystallised twice from hot water, the *acid* (D) being obtained in prisms, m. p. 183—185° (Found : C, 61·6; H, 7·9. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%).

The yellow oil (X) (see p. 192) was suspended in hot water, and an excess of milk of lime added to the boiling solution. After removal of the insoluble calcium salts, the solution was concentrated and acidified. The brown oil precipitated was extracted with ether (5 times), the dried extract evaporated, and the residual oil (100 g.) esterified with methyl alcohol and sulphuric acid. The partly esterified oil (53 g.) was recovered and re-esterified. The ester (51 g.) was fractionated under diminished pressure (17 mm.), but no homogeneous fractions were obtained. The two fractions of lowest b. p., 90—105° and 105—120°, gave on hydrolysis with methyl-alcoholic potassium hydroxide a mixture of acids which partly crystallised. In each case the acid was dissolved in hot water, the solution made faintly alkaline with ammonia, calcium chloride added, and the solution boiled. A crystalline calcium salt separated and this, decomposed in the usual manner, gave *as*-dimethylsuccinic acid, m. p. 139—140° (alone and in admixture with an authentic specimen). The filtrate from the insoluble calcium salt gave on acidification and extraction with ether dimethylmalonic acid, decomp. 185—187° (alone and after admixture with another specimen).

*Preparation of* 1-*Amino*-1-*methyllongifane.*—*Longifolamide.* The acid chloride (b. p. 173°/20 mm.), prepared from longifolic acid (25 g.) and thionyl chloride, was dissolved in ligroin (b. p. 40—60°) (250 c.c.) and added during 2 hours to ligroin (500 c.c.), cooled in salt–ice and mechanically stirred, through which a rapid stream of ammonia was passing. After further passage of ammonia for 1 hour, the solution was kept over-night, the ligroin then decanted from the mixture of amide and ammonium chloride, water added, and the further quantity of ligroin which separated added to the first fraction. The aqueous layer, which contained much solid in suspension, was extracted with ether, and the ethereal extract combined with the residues remaining after evaporation of the ligroin. The extract was well washed with sodium hydroxide solution to remove unchanged acid (0·5 g.), dried, and evaporated. The brown oily residue was distilled in steam to remove nitrile (0·8 g.) (see below), and the heavy non-volatile oil, after drying in a vacuum, triturated with ligroin. The amide (15 g.), which remained as a colourless crystalline solid, was sufficiently pure for further experiments. The ligroin solution gave on evaporation a further quantity of crude amide (5·5 g.), which was suitable for conversion into the urethane. In methyl-alcoholic solution (*c*, 4·197) longifolamide was lævorotatory, $[\alpha]_{5461}$ − 20·5°.

The amide was converted very readily into *longifonitrile*, and this, under the ordinary conditions employed for the conversion of acid chlorides into amides, formed the main product of the reaction. The nitrile is a faintly yellow viscid oil, b. p. 145—150°/2 mm.; it was not obtained quite free from the amide (Found : C, 81·6; H, 10·5. $C_{14}H_{21}N$ requires C, 82·8; H, 10·3%). It was hydrolysed to the amide by heating with sulphuric acid (90%) at 65—70° for 17 hours.

The urethane (*loc. cit.*, p. 2657) was prepared more conveniently by the following modification of the method previously employed. To a well-cooled solution of the amide (5 g.) in methyl alcohol, bromine (1·6 c.c.) was added and then, in one portion, well-cooled sodium methoxide (Na, 2·7 g.; MeOH, 60 c.c.). The mixture was heated on the water-bath for 1½ hours and made faintly acid with acetic acid, and the methyl alcohol distilled off. After addition of water, the urethane was dissolved in ether, and the ether washed with potassium hydroxide solution, dried, and evaporated. The urethane, which crystallised rapidly, m. p. 66—71°, was recrystallised from dilute methyl alcohol, forming thin plates, m. p. 76—77°, $[\alpha]_{5461}$ − 11·1° (in methyl alcohol; *c*, 2·624) (Found : C, 71·7; H, 9·9. Calc. for $C_{15}H_{25}O_2N$ : C, 71·7; H, 10·0%).

1-*Amino*-1-*methyllongifane*. The urethane (10 g.) was heated with sodium amyloxide (Na, 5 g.) at 160° for 8 hours. The cooled solution after dilution with water was made acid with hydrochloric acid, and the amyl alcohol removed in steam. After addition of excess of sodium hydroxide the liberated base was distilled in steam, the distillate saturated with salt, the base extracted with ether, and the dried ethereal extract evaporated. 1-*Amino*-1-*methyllongifane* is a colourless viscid oil, b. p. 150°/18 mm., $[\alpha]_{5461}$ − 35·3° (in ethyl alcohol; *c*, 10·874) (Found : C, 80·7; H, 12·0. $C_{13}H_{23}N$ requires C, 80·8; H, 11·9%). The *hydrochloride* crystallised from dilute hydrochloric acid in prismatic needles, decomp. 280—282° (sintering at 258°) (Found : Cl, 14·9. $C_{13}H_{23}N,HCl$ requires Cl, 15·5%). The *nitrite* crystallised from aqueous sodium nitrite in needles, decomp. 132° (Found : N, 11·6. $C_{13}H_{23}N,HNO_2$ requires N, 11·7%). α- *and* β-*Acetyl derivatives*. The base, mixed with twice its volume of acetic anhydride, was boiled for 2 minutes; to the cooled solution, which deposited crystals, alcohol was added, and the mixture boiled. The solvent was removed in a vacuum over potassium hydroxide, and the residual solid, needles, m. p. 135—170°, extracted with ligroin (b. p. 40—60°). The residue, m. p. 180° (sintering at 170°), was crystallised twice from ethyl acetate; the α-*acetyl* derivative separated in fine needles, m. p. 191—192°, $[\alpha]_{5461}$ − 56·4° (in ethyl alcohol; *c*, 2·146) (Found : N, 6·1. $C_{15}H_{25}ON$ requires N, 6·0%). The ligroin solution on cooling deposited a solid, m. p. 173°, from which a further quantity of the α-acetyl derivative was obtained on crystallisation from ethyl acetate. Complete evaporation of the ligroin gave a somewhat gummy solid which, after fractional crystallisation from dilute methyl alcohol and finally from ligroin, gave the β-*acetyl* derivative in needles, m. p. 163—165° (Found : N, 6·1%). The 3 : 5-*dinitrobenzoate* crystallised from methyl alcohol in pale yellow needles, m. p. 199—200°; $[\alpha]_{5461}$ − 12·2° (in chloroform; *c*, 2·372) (Found : C, 61·8; H, 6·6. $C_{20}H_{25}O_5N_3$ requires C, 62·0; H, 6·5%). α- *and* β-*Methiodides*. The base (5 g.), methyl iodide (17·5 g.), sodium carbonate (7·5 g.), and water (20 c.c.) were heated on the water-bath under reflux in an apparatus provided with a mercury seal for 8 hours. After remaining over-night, the solution was saturated with potassium iodide, and the solid which separated collected. The α-*methiodide*, which was readily soluble in water, methyl alcohol, and chloroform, but only sparingly in benzene and ethyl acetate, crystallised from benzene–chloroform in prisms, m. p. 258—259° (Found : I, 35·3. $C_{16}H_{30}NI$ requires I, 35·0%). The original mother-liquor, from which the α-methiodide had been separated, gave on addition of sodium hydroxide solution a liquid methiodide (5 g.), which crystallised on keeping. This was heated under reflux with an excess of methyl iodide in the presence of sodium hydroxide, and the methiodide isolated by extraction with chloroform. The solid remaining after evaporation of the solvent was triturated with ethyl acetate; it then had decomp. 160—162° (sintering at 148°). After two crystallisations from benzene the β-*methiodide* was obtained in fine needles, decomp. 184°. It crystallised with $1H_2O$, which was not lost at 100° (Found : I, 33·4. $C_{16}H_{30}NI,H_2O$ requires I, 33·3%).

In an attempted degradation the β-methiodide (5 g.) was added to silver oxide (from $AgNO_3$, 3·5 g.) in water (50 c.c.) and shaken for 12 hours at 60°. The filtered solution was concentrated on the water-bath, and the residual oil distilled under diminished pressure (22 mm.); vigorous decomposition occurred and an oil distilled at 140—150°. This was dissolved in ether and then washed with dilute hydrochloric acid; the acid solution deposited a crystalline hydrochloride (1·2 g.), and a further quantity (2·6 g.) was obtained on evaporation. The *dimethylamino-hydrochloride* crystallised from dilute hydrochloric acid, in which it was somewhat sparingly soluble, in thin plates, m. p. above 280° (Found : C, 69·8; H, 11·4; Cl, 13·3. $C_{15}H_{27}N,HCl$ requires C, 69·9; H, 10·9; Cl, 13·4%). The α-methiodide, after conversion into the ammonium base, behaved similarly, but the yield of hydrochloride was somewhat smaller and there was a distinct odour of trimethylamine.

*Conversion of* 1-*Amino*-1-*methyllongifane into Hydrocarbons and Alcohol*.—To a mixture of 1-amino-1-methyllongifane (5 g.), phosphoric acid (5 g.), and water (100 c.c.) through which a rapid current of steam was passing, sodium nitrite (3 g.) in water (50 c.c.) was added during 2 hours. When no further oil passed over, the distillate was saturated with salt, and the oil (2·5 g.) extracted with ether. The acid solution gave on basification unchanged base (2 g.). The oil volatile in steam (6 g.) was distilled under diminished pressure (18 mm.), giving two fractions: (i) 120—130° (2·9 g. Found: C, 85·4; H, 11·6%), and (ii) 130—160° (2·5 g. Found: C, 82·1; H, 11·5%). The two fractions were combined and heated at 200° with potassium hydrogen sulphate, and the recovered oil distilled over sodium (twice); the *hydrocarbon* then had b. p. 124°/20 mm., $d_{25^\circ}^{25^\circ}$ 0·95; $n_D^{25^\circ}$ 1·4995, $[\alpha]_{5461}$ + 6·04° (in acetone; *c*, 18·222) (Found: C, 88·0; H, 11·9. $C_{13}H_{20}$ requires C, 88·6; H, 11·4%). The hydrocarbon, which had an odour resembling that of longifolene, was a mixture, since titration with camphoric acid peroxide gave only 54·8% of unsaturation. With hydrogen chloride in ethereal solution at 0° it gave a liquid *hydrochloride* (Found: Cl, 12·6. $C_{13}H_{21}Cl$ requires Cl, 16·7%). The higher-boiling alcohol fraction (see above) did not react with phthalic anhydride at 110—120° and it could not be dehydrated with either naphthalene-β-sulphonic acid or the Grignard reagent.

*Oxidation of the Hydrocarbon Mixture.*—(i) *With potassium permanganate.* The hydrocarbon (4 g.), sodium hydroxide (1 g.) in water (10 c.c.), potassium permanganate (7·2 g.) and ice (400 c.c.) were shaken for 10 hours, much permanganate still remaining unattacked. This was reduced with sulphur dioxide. The unchanged hydrocarbon and oxidation products were extracted from the clear solution with ether, the acids removed with sodium carbonate, and the ether dried and evaporated; the hydrocarbon (3 g.) then remained. The sodium carbonate solution on acidification gave a viscid oil, which was dissolved in ether and, after removal of the solvent, ground (0·9 g.) with formic acid; a crystalline solid then separated. The *acid* (F) crystallised from formic acid in thin leaflets which under the microscope were seen to consist of perfectly formed, equilateral triangles, m. p. 235—236° (Found: C, 65·0; H, 8·5. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·3%). On digestion with acetyl chloride the acid gave a liquid anhydride, which was insoluble in cold sodium hydroxide solution and only slowly dissolved on warming, with formation of the sodium salt of the acid. The original formic acid solution, from which the acid (F) had been separated, was evaporated in a vacuum over potassium hydroxide, and the oil digested with acetyl chloride for 2 hours. After removal of the excess of acetyl chloride the residue was ground with sodium carbonate solution, a pasty mass remaining undissolved. This was rendered to ether, the extract dried, and the solvent evaporated. The partly crystalline residue was ground with methyl alcohol, and the solid collected and recrystallised from methyl alcohol and then from benzene–ligroin; the *lactone* was thus obtained in thin leaflets, m. p. 190° (Found: C, 73·7; H, 9·1. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%). The lactone was sparingly soluble in hot water and only very slowly in hot sodium hydroxide solution, which on acidification gave an acid which was not obtained crystalline. The methyl-alcoholic solution from which the lactone had been removed gave a further quantity of the acid (F).

(ii) *With ozone.* Ozone was passed through a solution of the hydrocarbon (3 g.) in ethyl acetate (20 c.c.), cooled in acetone–carbon dioxide, until the issuing gas liberated iodine from potassium iodide–boric acid solution. After addition of palladium-norite (1 g.) the ethyl acetate solution was shaken with hydrogen until no further absorption took place (130 c.c.; 8 hours); the filtered solution was then washed with water. The aqueous extract contained formaldehyde (dimedone test). The products from several such oxidations were combined, the ethyl acetate evaporated, the residue dissolved in ether, the ethereal extract washed with potassium hydroxide solution (which removed an acid giving a liquid sparingly soluble potassium salt) and dried, and the solvent removed. The residual oil, which had a strong camphoraceous odour, was distilled in steam, and the volatile oil isolated by ether and distilled under diminished pressure (22 mm.), whereby it was readily separated into two main fractions: (i) 120—130° and (ii) 130—150°. Fraction (i), distilled over sodium (twice), had b. p. 125—127°/25 mm., $d_{25^\circ}^{25^\circ}$ 0·9514, $n_D^{24^\circ}$ 1·4967, $[\alpha]_{5461}$ + 18·8° (in ethyl acetate; *c*, 17·10) (Found: C, 88·2; H, 11·8. $C_{13}H_{20}$ requires C, 88·6; H, 11·4%). The tetracyclic hydrocarbon, 1-*methyldehydrolongifane*, had a pleasant odour and in alcoholic solution gave no colour with tetranitromethane. With hydrogen chloride in ethereal solution at 0° it gave a liquid *hydrochloride* (Found: Cl, 13·5. $C_{13}H_{21}Cl$ requires Cl, 16·9%). The higher-boiling fraction (ii) was redistilled, two fractions being obtained: (a) a mobile camphoraceous oil, b. p. 130—140°/22 mm., and (b) a viscid yellow oil, b. p. 140—160°/22 mm. Fraction (a) gave with semicarbazide acetate a *semicarbazone*, which crystallised from dilute methyl alcohol in matted needles, m. p. 208—209° (Found: C, 66·8; H, 9·1. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 8·9%). For the preparation of the hydroxymethylene derivative the ketone (2·1 g.) in ether containing sodium (0·6 g.) in suspension was treated with amyl formate (1·4 g.) at 0°. After remaining over-night, the excess of sodium was dissolved by the addition of ice, the aqueous alkaline layer separated, extracted with ether to remove neutral oil, and acidified with acetic acid. The viscid oil which separated was dissolved in ether, dried, and recovered. The liquid hydroxymethylene derivative gave in alcoholic solution an intense purple-red colour with ferric chloride and a sparingly soluble copper salt with copper acetate. The *semicarbazone* separated from benzene–methyl alcohol as a micro-crystalline powder, m. p. 199° (Found : N, 15·7. $C_{14}H_{21}O_2N_3$ requires N, 16·0%). The 2 : 4-dinitrophenylhydrazone was an amorphous red powder. Fraction (b) (see above) gave a gummy semicarbazone, but the 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in terracotta needles, m. p. 250—251° (Found : C, 63·0; H, 4·1%). The nature of this ketone was not determined.

The potassium hydroxide solution (see above) was acidified, the acid rendered to ether, and the solvent removed. The liquid acid, which gave an amorphous 2 : 4-dinitrophenylhydrazone, was dissolved in sodium hydroxide solution and treated at 0° with an excess of sodium hypobromite, bromoform being deposited. The recovered liquid acid was digested with acetyl chloride and, after removal of the excess of acid chloride, the oil was dissolved in ether and the ethereal extract washed with sodium hydroxide solution (which removed resinous acids), dried, and evaporated. The oil crystallised when ground with methyl alcohol, and the solid was recrystallised from this solvent and then from ligroin–benzene, from which it separated in conglomerates of prismatic needles, m. p. 166° (Found: C, 71·6; H, 8·1%). The *acid* (G) prepared by digestion of this substance with alkali crystallised from water in prisms, m. p. 132° (Found : C, 66·3; H, 7·8%).

*Oxidation of* 1-*Amino*-1-*methyllongifane with Potassium Permanganate.*—To a solution of the base (5 g.) in acetone (75 c.c.) maintained at 30—35°, potassium permanganate (16 g.) was added gradually with mechanical stirring. The manganese dioxide sludge was filtered off and washed with acetone, and the acetone solution, after removal of excess of permanganate with sulphur dioxide, evaporated. When an ethereal solution of the residual oil was washed with dilute sulphuric acid to remove unchanged base (1 g.), a small quantity of a crystalline solid (Z) separated at the interface. This was removed, and the ethereal extract dried and evaporated, leaving an oil (2·7 g.) which partly solidified. After admixture with ligroin the solid (1·2 g.) was collected and recrystallised (twice) from ethyl acetate; it then had m. p. 191—192°, both alone and after admixture with α-1-acetamido-1-methyllongifane [Found : C, 76·4; H, 10·8; N, 6·2; *M* (Rast), 206. Calc. for $C_{15}H_{25}ON$ : C, 76·6; H, 10·6; N, 6·0%; *M*, 235]. The substance (Z) crystallised from alcohol, in which it was very sparingly soluble, in needles, m. p. above 280°. It contained sulphur and was possibly the sulphate of the base (Found : N, 5·8. $C_{26}H_{50}O_4N_2S$ requires N, 5·8%). The manganese dioxide sludge was suspended in water, and sulphur dioxide passed through until all the dioxide had dissolved; a gummy acid remained in suspension. This was dissolved in ether, the dried solution evaporated, and the viscid oil (1·9 g.) which remained dissolved in dilute aqueous ammonia; addition of barium chloride then precipitated a sparingly soluble barium salt. The filtrate contained a small quantity of a gummy acid, which was not examined. The barium salt was decomposed; the *acid* (E) (0·8 g.) isolated by ether, separated as a somewhat gummy solid, which was crystallised from dilute acetic acid or dilute methyl alcohol and obtained in serrated prisms, containing solvent of crystallisation which was lost on drying over phosphoric oxide in a vacuum; m. p. 122—124° (sintering at 110°), $[\alpha]_{5461}$ − 58·7° (in ethyl alcohol; *c*, 0·324) (Found : C, 69·2; H, 9·1; N, 5·2; *M*, 280. $C_{16}H_{25}O_3N$ requires C, 68·8; H, 9·0; N, 5·0%; *M*, 281). The acid, which was insoluble in mineral acids and did not reduce Fehling's solution, gave a sparingly soluble sodium salt, which crystallised in needles; with semicarbazide acetate a *semicarbazide* was obtained crystallising from methyl alcohol in conglomerates of needles, decomp. 179—180° to an opaque oil, which cleared with further decomp. at 248—249° (Found : C, 58·0; H, 8·8. $C_{17}H_{30}O_4N_4$ requires C, 57·6; H, 8·5%). The semicarbazide was decomposed by dilute hydrochloric acid, yielding the parent acid. When the acid (0·55 g.) was heated at 160°, vigorous evolution of carbon dioxide occurred and a gum remained which, when mixed with dilute potassium hydroxide solution, was converted into a white powder. After crystallisation from ligroin (b. p. 60—80°) (twice) the *substance* separated in soft needles, m. p. 144°, $[\alpha]_{5461}$ − 69·8° (in ethyl alcohol; *c*, 1·146) (Found : C, 76·9; H, 10·8. $C_{15}H_{25}ON$ requires C, 76·6; H, 10·6%). The substance (0·2 g.) was mixed with alcoholic sulphuric acid (10 c.c. of 10%) and heated on the water-bath for 6 hours. After addition of water the solution was made alkaline and extracted with ether, and the extract washed with water to remove alcohol, dried, and evaporated. The base so obtained, which gave a sparingly soluble hydrochloride, was acetylated with acetic anhydride, and the acetyl derivative crystallised from ethyl acetate; it had m. p. 191—192°, both alone and after admixture with α-1-acetamido-1-methyllongifane.

We are indebted to Mr. P. H. Guest, Manager, the Turpentine Factory, Jallo, for a gift of the longifolene used and to the Government Grants Committee of the Royal Society, the Chemical Society, and Imperial Chemical Industries Ltd. for grants.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, November* **24*th*, 1933.**]