184. *Usnic Acid. Part V.*

By Frank H. Curd and Alexander Robertson.

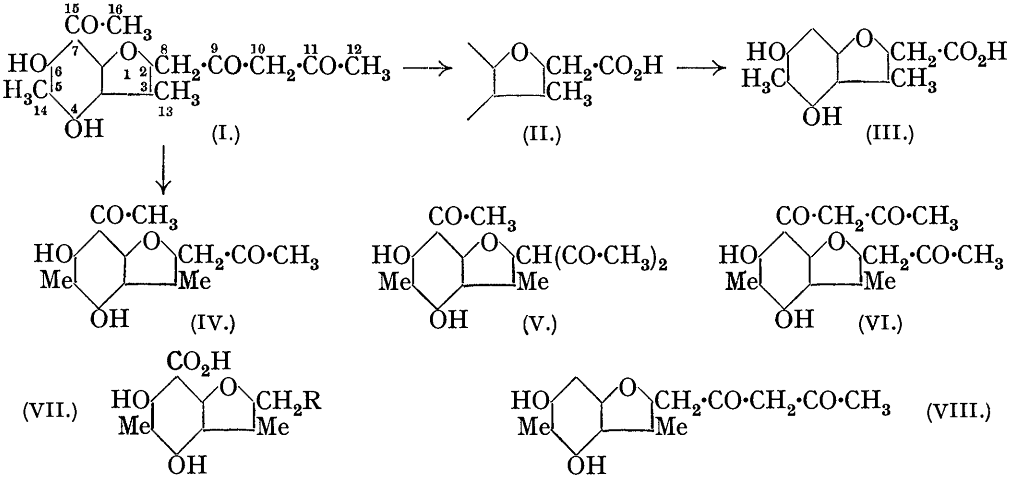
The experiments described in the present communication were carried out in 1932—33, and, although our studies on usnic acid are not yet completed, it is necessary, in view of the work of Asahina and Yanagita (*Ber.*, 1936, **69**, 1646), to place the results on record and to discuss their bearing on revised expressions possible for decarbousnic acid, decarbousnol, usnolic acid, and usnic acid. Until decisive evidence regarding the structures proposed in Part III (J., 1933, 1173) for pyrousnic acid and usnetic acid became available (Asahina and Yanagita, *loc. cit.*; Part IV, J., 1936, 1834) this discussion on new formulations for these compounds did not appear profitable.

Decarbousnic Acid.

This compound is the main product of the reaction obtaining when usnic acid is heated with 96% alcohol under pressure (compare Paternò, *Gazzetta*, 1876, **6**, 113; Widman, *Annalen*, 1900, **310**, 230, 265; 1902, **324**, 139) and, although the reaction mechanism involved is still obscure, the process is regarded as being essentially one of hydration and simultaneous loss of carbon dioxide. Whilst structures of the hemi-quinonoid type proposed for usnic acid and its degradation products by Schöpf and Heuck (*Annalen*, 1927, **459**, 233) are fundamentally unsound (compare Part III, J., 1933, 1173), the suggestion of these authors that decarbousnic acid contains the groups CH_3·CO· and :C·CO·CH·CO·C: and is not a carboyxlic acid affords a basis for a satisfactory explanation of its behaviour. Thus decarbousnic acid cannot be esterified or decarboxylated and the oxime anhydride, anhydrobisphenylhydrazone, and anilide described by Widman (*loc. cit.*) may be considered to be respectively *iso*oxazole, pyrazole, and anil derivatives. The presence of a 1 : 3-diketonic group in this compound also receives support from the fact that the product formed by interaction with semicarbazide hydrochloride has now been found to have the composition of a pyrazole derivative and not that of a hydrazone as Widman (*loc. cit.*) suggested. In this respect the behaviour of decarbousnic acid is strictly analogous to that of benzoylacetophenone (Posner, *Ber.*, 1901, **34**, 3973).

With a view to obtaining confirmatory evidence of the presence of a 1 : 3-diketonic group in decarbousnic acid we have investigated the hydrolysis of the compound with warm aqueous potassium hydroxide and by this procedure have obtained acetic acid, acetone, usnetic acid (II), pyrousnic acid (III), and a compound $C_{15}H_{16}O_5$, and we have also observed that the particular combination of these products which can be conveniently detected in the reaction mixture is to some extent dependent on the conditions employed. Since it apparently arises from decarbousnic acid by loss of an acetyl group, the substance $C_{15}H_{16}O_5$ has been designated *deacetyldecarbousnic acid.* It is of interest to note that with the exception of this compound and of usnetinic acid (Part III, *loc. cit.*) the products of the hydrolytic fission of decarbousnic acid are identical with those formed from usnic acid under comparable conditions and, although so far as we are aware—and our own observations confirm this—decarbousnic acid has never been obtained from usnic acid by hydrolytic fission with warm aqueous sodium or potassium hydroxide, the present results suggest that it may be an intermediate stage in this degradation.

The behaviour of decarbousnic acid on hydrolysis in conjunction with the nature of the products formed with ketonic reagents affords conclusive evidence that this compound is a 1 : 3-diketone which may be regarded as being derived from usnetic acid by the addition of acetone with the elimination of the elements of water and the suppression of the carboxyl group (*i.e.*, the reversal of one type of hydrolysis) and thus, in agreement with the suggestion of Asahina and Yanagita (*loc. cit.*), may be represented by the formula (I).



The expression (I) can be justified experimentally in every detail and, apart from the formation of decarbousnol which will be discussed later, affords a satisfactory explanation of the main properties and reactions of decarbousnic acid.

(1) Decarbousnic acid obtained from *d*- or *l*-usnic acid is always optically inactive and therefore presumably does not contain an asymmetric carbon atom, a conclusion which is supported by the fact that Schöpf and Heuck (*loc. cit.*) observed that *d*-diacetylusnic acid also gave rise directly to an inactive diacetyl derivative of decarbousnic acid.

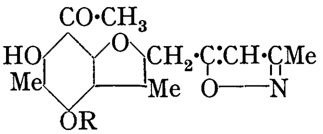
(2) The behaviour of the compound on titration as a dibasic acid is explained by the presence of an acidic enolic group * and of the phenolic hydroxyl group in the 4-position, the acidity of which is enhanced by the *C*-acetyl group in the 7-position.

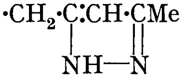
(3) Formula (I) affords a satisfactory explanation of the behaviour of decarbousnic acid with ketonic reagents. The *iso*oxazole and pyrazole derivatives obtained by oximation and by the action of semicarbazide hydrochloride (compare Posner, *loc. cit.*) may be

* Two structures are possible for the enolic form of a diketone of the type (I), *viz.*, (A) $R{\cdot}CH_2{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_3$ and (B) $R{\cdot}CH_2{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CH_3$ [$R{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}C(OH){:}CH_2$ is unlikely], and similarly there are two possible formulæ for the *iso*oxazole and pyrazole derivatives, depending on whether decarbousnic acid reacts as (A) or (B). Only one set of formulæ is employed in the present communication, although it is recognised that the respective alternative structures are equally possible.

represented by formula type (IX, R = H) and (X, R = H) respectively, whilst the anilide of Widman is the anil type (XI, R = H).

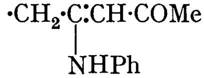
(IX.)



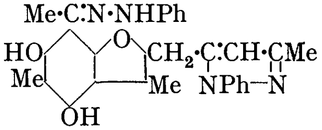


(X.)

(XI.)



$\cdot CH_2\cdot C(NHPh){:}CH\cdot COMe$

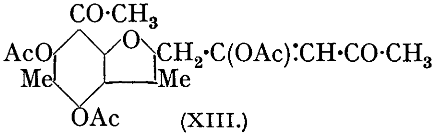


(XII.)

By heating the *iso*oxazole (oxime anhydride) with acetic anhydride, Widman (1900) obtained a monoacetyl derivative which was insoluble in aqueous sodium hydroxide but gave a green ferric reaction. Since it is well known that in a compound of the type (IX, R = H) the hydroxyl group at the 4-position is preferentially acylated or methylated, Widman's acetate must have formula type (IX, R = Ac), a view which is in agreement with the fact that the behaviour of the acetate towards sodium hydroxide and alcoholic ferric chloride is similar to that of usnetol monomethyl ether and of methyl 4-*O*-methylusnetate (Part III, *loc. cit.*).

In the condensation of decarbousnic acid with phenylhydrazine both the 1 : 3-diketonic and the 7-acetyl groups react, giving rise to an anhydrobisphenylhydrazone which must have the pyrazole structure type (XII).

(4) Mono-, di-, tri-, and tetra-acetyl derivatives of decarbousnic acid (Widman, *loc. cit.*; Schöpf and Heuck, *loc. cit.*) have been described and, although it is not possible at present to allocate definite formulæ to the mono- and the di-acetyl derivative, the triacetyl compound, which has a negative ferric reaction, has presumably the structure type (XIII), whereas the golden-yellow tetra-acetyl derivative may be of the type (XIV) or (XV).



(XIII.)

$\cdot CH{:}C(OAc)\cdot CH{:}C(OAc)\cdot CH_3$

(XIV.)

$\cdot CH{:}C(OAc)\cdot CH(CO\cdot CH_3)_2$

(XV.)

(5) The structure (I) for decarbousnic acid provides a rational explanation of the formation of the products of hydrolysis, including deacetyldecarbousnic acid. Although the latter compound, which sublimes unchanged in a high vacuum, behaves on titration as a monobasic acid, it does not contain a carboxyl group and does not dissolve in aqueous sodium bicarbonate or react with warm aniline. On the basis of the expression (I) for decarbousnic acid the deacetyl derivative may be represented by formula (IV), whereby its behaviour as a monobasic acid on titration is accounted for by the enhanced acidity of the phenolic hydroxyl group at the 4-position due to the presence of the *C*-acetyl group at the 7-position. This formulation is in agreement with the fact that the compound gives the same characteristic ferric reaction as usnetic acid and usnetol (Part III, *loc. cit.*) and forms a diacetate which is insoluble in aqueous sodium hydroxide and has a negative ferric reaction. The alternative structure (VIII) for deacetyldecarbousnic acid is excluded because a compound of this type would be expected to give the red or red-brown ferric reaction characteristic of the group $\cdot CO\cdot CH_2\cdot CO\cdot$ (the pyrousnyl residue does not give a coloration with alcoholic ferric chloride; Part III, *loc. cit.*) and to form an *O*-diacetyl derivative soluble in aqueous sodium hydroxide.

In the conversion of usnic acid into decarbousnic acid Widman (*loc. cit.*) obtained a by-product, m. p. 197°, which he considered to be an isomeride of the latter and named *iso*decarbousnic acid. This substance, which in one experiment was the main product of the reaction, has been found to be deacetyldecarbousnic acid (IV).

The alternative possible formulæ, (V) and (VI), for decarbousnic acid which also embody a 1 : 3-diketonic group can be excluded from a consideration of the behaviour of the compound on hydrolytic fission. Although both the expressions (V) and (VI) can account for the formation of deacetyldecarbousnic acid (IV), neither is compatible with the formation of usnetic acid (II) and of pyrousnic acid (III) ; *e.g.*, the products of the alkaline hydrolysis of (VI) would not be usnetic acid and pyrousnic acid but their respective isomerides (VII, R = Ac) and (VII, R = H), whereas compounds of this type have never been encountered among the degradation products of decarbousnic acid or of usnic acid.

Usnic Acid.

The formulation of this compound may be expressed as a reversal of the process obtaining in the formation of decarbousnic acid, *i.e.*, by the addition of a carboxyl group with the elimination of the elements of water. Apart from the formation of usnolic acid (compare decarbousnol) the main criteria which must be satisfied by any formula for usnic acid may be grouped as follows :—

(1) Usnic acid contains an asymmetric carbon atom which appears to be destroyed in the conversion of usnic acid into the isomeride usnolic acid and into decarbousnic acid.

(2) The view expressed by Schöpf and Heuck that the acidic properties of usnic acid are due to the presence of a highly acidic enolic group as in decarbousnic acid is an essential feature. Although it does not appear to contain a carboxyl group, usnic acid titrates as a monobasic acid, a phenomenon which can hardly be explained by the opening of a lactone ring because we have found that acidification of a solution of the *l*-isomeride in dilute aqueous sodium hydroxide, which has been kept for a short time, gave unchanged material, having the initial rotatory value. This view is also strongly supported by the fact that Schöpf and Heuck (*loc. cit.*) found that deacetylation of *d*-diacetylusnic acid with hot dilute aqueous sodium hydroxide yielded *d*-usnic acid.

(3) According to the Zerewitinoff method usnic acid contains three active hydrogen atoms (Schöpf and Heuck, *loc. cit.*), and, although in a compound of this type conclusions drawn from Zerewitinoff determinations cannot be relied on entirely, this result is supported by the fact that the diacetyl derivative behaves on titration as a monobasic acid and gives a wine-red ferric reaction. Although a phenolic hydroxyl group in the *o*-position to a carbonyl group would account for the coloration with alcoholic ferric chloride, this group would exhibit an abnormally low acidity due to chelation and therefore these results suggest that diacetylusnic acid and consequently usnic acid contain an acidic enolic group, thus rendering unnecessary the assumption that the behaviour of these compounds on titration is due to the opening of a lactone ring system.

(4) In addition to forming a normal oxime, a semicarbazone, and a phenylbenzylhydrazone, usnic acid yields an oxime anhydride and an anhydrobisphenylhydrazone (Widman, *loc. cit.* ; Schöpf and Heuck, *loc. cit.*), whereby it closely resembles decarbousnic acid. On the view that usnic acid contains a lactone group the last two derivatives might well be an *iso*oxazolone and a pyrazolone, respectively derived from a potential β-ketonic acid, but the production of compounds of this type implies a complex change involving the opening of the lactone ring system with subsequent dehydration of the resulting *iso*oxazolone and pyrazolone. It would appear to be more likely that, as in the case of the corresponding decarbousnic acid derivatives, the oxime anhydride and anhydrobisphenylhydrazone of usnic acid are respectively *iso*oxazole and pyrazole derivatives, implying the presence of a 1 : 3-diketonic system in the molecule (compare Asahina and Yanagita, *loc. cit.*). Further, both carbonyl groups of this residue cannot be present in a ring system, because compounds like the alkyl- and phenyl-dihydroresorcinols have been shown by Vorländer (*Annalen*, 1897, **294**, 253) to form normal mono- and di-oximes and do not give *iso*oxazoles, and the phenylhydrazone of ethyl dihydroresorcylate cannot be converted into a pyrazole derivative (Knoevenagel, *Ber.*, 1894, **27**, 2343).

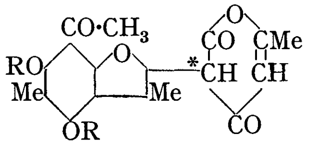
The presence of a β-ketonic group in usnic acid also accounts for the formation of an anil (the anilide of Widman, *loc. cit.*). Since this derivative has been obtained in *d*-, *l*-, and racemic forms and the anhydrobisphenylhydrazone in the *d*- and racemic forms, the enolisation of the diketonic group on which their formation depends does not involve the asymmetric carbon atom.

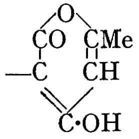
(5) With the exception of deacetyldecarbousnic acid and usnetinic acid the products of the hydrolytic fission of usnic acid with alkali are identical with those obtained from decarbousnic acid.

(6) Although a lactone group has been considered to be an essential feature of the usnic acid molecule (Widman; Schöpf and Heuck; Asahina and Yanagita, *locc. cit.*), it must be emphasised that, apart from the conversion of usnic acid into the isomeride usnolic acid, the mechanism of which is still obscure, there is no satisfactory evidence indicating the presence of this group and it may well be that the >CO group, which is eliminated in the conversion of usnic acid into decarbousnic acid and which appears as the carboxyl group of usnolic acid (see section on Usnolic Acid), is originally present as a ketonic and not as a lactone group. The experiments on the deacetylation of diacetylusnic acid by Schöpf and Heuck (*loc. cit.*) and our own observations on the action of cold aqueous sodium hydroxide on usnic acid indicate that the lactone group if present is either stable to alkali under those conditions or is instantaneously re-formed on liberation of the parent acid from the sodium salt.

On the view that usnic acid is a lactone derived from decarbousnic acid it would seem likely, since decarbousnic acid does not contain an asymmetric centre and on this view would in all probability be formed by the hydration of the lactone group and subsequent loss of carbon dioxide, that, in the system $:C_{\alpha}\cdot C_{\beta}O\cdot O\cdot C_{\gamma}:$, C_{α} is the asymmetric centre and not C_{γ}. Accordingly, structures which do not have this type of formulation need not be considered; thus formulæ which have the lactone group attached at the 12-, 13-, 14-, or 16-position of decarbousnic acid (I) are excluded. Of the remaining possibilities, *viz.*, the attachment of the lactone group at the 8- or 10-position of (I), the latter implies a β-lactone structure and the former leads to the formulation of usnic acid as a pyronone (XVI, R = H) where the carbon atom at the 3-position (marked *) is asymmetric, a structure which has been proposed by Asahina and Yanagita (*loc. cit.*).

(XVI.)





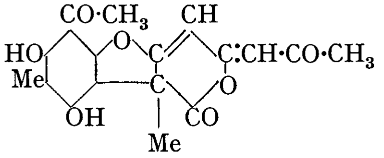
(XVII.)

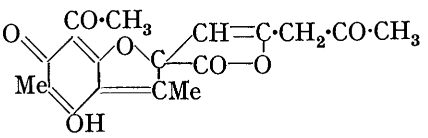
Although the expression (XVI, R = H) for usnic acid accounts for the products formed by alkaline hydrolysis and the formation of decarbousnic acid, it fails to explain the behaviour of the compound as a 1 : 3-diketone in forming an oxime anhydride and an anhydrobisphenylhydrazone without assuming a complex change which is difficult to formulate. Further, a compound having a pyronone type of structure (XVI, R = H) would be expected to exist in the enolic form (XVII, R = H) (*e.g.*, compare 4-hydroxy coumarins) and in any case, if the compound were normally obtained in the ketonic form, enolisation with consequent loss of optical activity would take place in the presence of aqueous sodium hydroxide. Moreover, the properties, *viz.*, titration as a monobasic acid and red ferric reaction, of the diacetate, which on this formulation would presumably be (XVI, R = Ac), indicate the presence of an enolic group. On these grounds, therefore, the expression (XVI, R = H) for usnic acid is regarded as untenable.

In attempting to deduce a new formulation for usnic acid embodying the essential properties enumerated in sections 1—6 inclusive (pp. 897—898), we have considered the question as to whether the molecule contains the benzofuran residue of usnetic acid and, though the evidence at our disposal clearly indicates that the benzofuran skeleton is intact in usnic acid, this system may exist in a modified form as in formulæ (XVIII), (XIX), and (XX, R = H).

Of these, the expression (XX, R = H), which retains the 1 : 3-diketonic system of decarbousnic acid, accounts for the following properties of usnic acid : optical activity, titration as a monobasic acid due to an acidic enolic group, behaviour with ketonic reagents, formation of the products of hydrolysis, and the conversion into decarbousnic acid by opening of the lactone ring and the extrusion of the carboxyl group due to the tendency of the system to revert to the more stable benzofuran type (I). In formulating the acidic diacetyl derivative on the basis of the structure (XX, R = H) it is necessary to assume that one of the acetyl groups is attached to a carbon atom of the 1 : 3-diketonic system as in (XX, R = Ac), an expression which would also account for the acidic properties and the ferric reaction due to the presence of an enolic group. It is less easy, however, to explain the deacetylation of this diacetyl compound by warm dilute aqueous sodium hydroxide with the recovery of unchanged usnic acid (Schöpf and Heuck, *loc. cit.*), because it is unlikely on stereochemical grounds that the lactone ring system in (XX) has a stability comparable with that of an α-coumaranone.

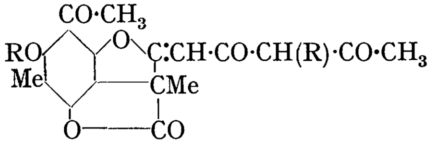
(XVIII.)





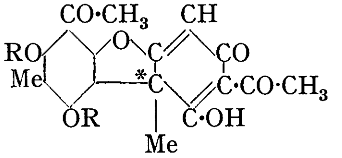
(XIX.)

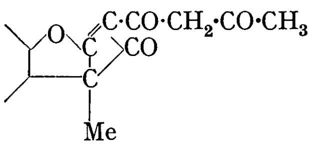
(XX.)



Although on the evidence which is available at present formula (XX, R = H) is clearly a more satisfactory expression for usnic acid than (XVI, R = H) it seems desirable, in view of the aforementioned deficiencies of (XX, R = H), to consider the alternative possibility, *viz.*, that usnic acid does not contain a lactone group. This implies that the $>$CO group of usnic acid, which is lost on conversion of the compound into decarbousnic acid, is originally present as a ketonic and not as a lactone group. On this view we may formulate usnic acid as (XXI, R = H) or (XXII, R = H), of which only the former need be considered at present. This structure, where ring C is a *gem*-substituted phloroglucinol residue similar to that present in filicinic acid and its derivatives (J., 1933, 1617), would account for the optical activity of usnic acid, the products obtained on hydrolysis, the behaviour with ketonic reagents and with aniline, the presence of three active hydrogen atoms as indicated by the Zerewitinoff method, and the properties of the diacetate, which presumably would be (XXI, R = Ac).

(XXI.)





(XXII.)

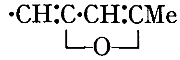
Whilst by analogy with decarbousnic acid a compound of the type (XXI, R = H) might be expected to titrate as a di- and not as a mono-basic acid, a more serious objection to the structure (XXI, R = H) is the difficulty of explaining the conversion of usnic acid and its diacetate, respectively, into decarbousnic acid and diacetyldecarbousnic acid (Schöpf and Heuck, *loc. cit.*). To account for this reaction it is necessary to assume, as is not unreasonable, that the asymmetric carbon atom (marked *) accommodating the angular methyl group is a centre of weakness.

The available experimental evidence does not allow us to make a clear decision between the two types of structure (XX, R = H) and (XXI, R = H) which appear possible for usnic acid but it is of interest to note that the latter formula is derived by the union of two identical *C*-methylphloracetophenone units and is related to the diphenyl ether residue of the depsidone type of lichen acid.

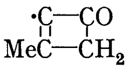
Decarbousnol and Usnolic Acid.

The formation of decarbousnol by dehydration of decarbousnic acid with concentrated sulphuric acid and the isomerisation of usnic acid to usnolic acid by the same reagent have been confirmed (compare Paternò, *Gazzetta*, 1900, **30**, 109; Widman, *loc. cit.*). Though the expression (I) for decarbousnic acid does not offer a clear explanation of the former reaction, for which we have been unable to find an analogy in the literature, there appear to be four possible ways in which the dehydration product of a 1 : 3-diketone of this type may be expressed, *viz.*, (XXIII), (XXIV), (XXV) and (XXVI), of which (XXV) is regarded as highly improbable.

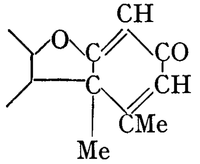
(XXIII.)



$\cdot CH{:}C\cdot CH{:}CMe$ (with $-O-$ bridging)



(XXIV.)



(XXVI.)

(XXV.) $\cdot CH_2\cdot C\vdots C\cdot COMe$

The remaining structures account for the following properties of decarbousnol: behaviour as monobasic acid on titration, inability to form an anil owing to the suppression of the 1 : 3-diketonic group, the green ferric reaction, and the formation of a monoacetyl derivative which is almost insoluble in aqueous sodium hydroxide but gives a blue-green ferric reaction.

Usnolic acid, which behaves on titration as a dibasic acid, contains one carboxyl group and forms monomethyl and monoethyl esters, both of which yield normal mono-oximes (compare Widman, *loc. cit.*). On decarboxylation this acid has now been found to yield decarbousnol, thereby clarifying the relationship of the two compounds. This result, together with the conversion of usnolic acid into the anil of decarbousnic acid by means of warm alcoholic aniline (Widman, *loc. cit.*), which we have confirmed, affords clear proof that the carbon atom which is lost in the degradation of usnic acid to decarbousnic acid appears as the carboxyl group of usnolic acid. Further, the interaction of the potential 1 : 3-diketonic group of usnolic acid with aniline is clearly dependent on the presence of the carboxyl group, because decarbousnol cannot be induced to react with aniline under similar conditions (compare Widman, *loc. cit.*). In connexion with this reaction it is of interest to note that the anil of phenyldihydroresorcylic acid is readily decarboxylated (Vorländer, *Annalen*, 1897, **294**, 253) under conditions similar to those employed in the conversion of usnolic acid into the decarbousnic acid anil.

EXPERIMENTAL.

Deacetyldecarbousnic Acid.—This compound was isolated in the course of the preparation of decarbousnic acid according to Widman's procedure (*Annalen*, 1900, **310**, 265). A mixture of usnic acid (5 g.), 96% alcohol (20 c.c.), and ether (1 c.c.) was heated in a sealed tube at 150—160° for 6 hours, more alcohol was added to the reaction mixture, and the resulting solution was evaporated in a vacuum at room temperature. The crystalline material which separated first consisted of almost pure decarbousnic acid (2·8 g.) and on recrystallisation from alcohol formed clusters of pale yellow needles, m. p. 178—179° (Found : C, 64·3; H, 5·9. Calc. for $C_{17}H_{18}O_6$: C, 64·2; H, 5·7%). On being heated, the brilliant yellow solution of this compound in sulphuric acid becomes red, then brown, and finally purple-brown.

Semicarbazide hydrochloride (0·3 g.), dissolved in a little water, was added to a hot alcoholic solution of decarbousnic acid (0·5 g.), and the mixture heated on the water-bath for ½ hour. On isolation the *pyrazole* derivative separated from benzene, containing a little alcohol, in clusters of colourless needles, m. p. 237—238° [Found : C, 65·3; H, 6·1; N, 9·0. $C_{17}H_{18}O_4N_2$ (pyrazole) requires C, 65·0; H, 5·7; N, 8·9%. Calc. for $C_{17}H_{20}O_5N_2$ (hydrazone) : C, 61·4; H, 6·0; N, 8·4%. Calc. for $C_{18}H_{19}O_5N_3$ (semicarbazone) : C, 60·5; H, 5·3; N, 11·8%] (Widman, *Annalen*, 1900, **310**, 275, gave m. p. 237° for a compound obtained in a similar manner which he considered to be a hydrazone).

Evaporation of the liquors left after the separation of decarbousnic acid gave crystals of *deacetyldecarbousnic acid* (0·3 g.); a further quantity (0·25 g.) was obtained by concentration of the mother-liquor from the first crystallisation of crude decarbousnic acid. Purified from alcohol, this compound formed colourless, feathery laminæ, m. p. 199—200°, which gave a greenish-purple to purple-blue coloration with alcoholic ferric chloride (Found : C, 65·3; H, 5·8. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%). On titration with 0·1*N*-sodium hydroxide it behaves as a monobasic acid, forming a yellow solution (0·1099 g. required 4·0 c.c. of 0·1*N*-sodium hydroxide, giving *M*, 275. $C_{15}H_{16}O_5$ requires *M*, 276). The colorations given by deacetyldecarbousnic acid with hot sulphuric acid are very similar to those obtained with decarbousnic acid except that on addition of water the final purple-brown colour is not discharged. On being treated with sulphuric acid under conditions whereby the latter substance is converted into decarbousnol (see below), deacetyldecarbousnic was recovered unchanged.

In one experiment on the preparation of decarbousnic acid the contents of the tube were not a thick jelly as described in the literature but consisted of masses of hard crystals which on isolation proved to be deacetyldecarbousnic acid, m. p. and mixed m. p. 199—200° after recrystallisation (Found : C, 65·3; H, 5·8%). A further small quantity of the same product was obtained from the alcoholic liquors, but decarbousnic acid could not be detected.

Treatment of the deacetyldecarbousnic acid (0·5 g.) with acetic anhydride (1 c.c.) and pyridine (3 c.c.) at 37° for 24 hours gave the *diacetate*, which separated from ethyl acetate–light petroleum and then dilute methyl alcohol in clusters of needles, insoluble in aqueous sodium hydroxide and having a negative ferric reaction; m. p. 146—147° (Found : C, 62·9; H, 5·8. $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%).

Hydrolytic Fission of Decarbousnic Acid.—The following are typical of the results obtained : (A) The compound (2 g.) was heated with a solution of potassium hydroxide (4 g.) in water (10 c.c.) at 170—180° in an atmosphere of hydrogen for 10 minutes, and the cooled reaction mixture acidified with dilute sulphuric acid. Crystallisation of the precipitate from alcohol gave deacetyldecarbousnic acid in characteristic feathery laminæ, m. p. 198—199°, identified by comparison with an authentic specimen.

Pyrousnic acid was isolated with absolute ether from the aqueous filtrate left on separation of deacetyldecarbousnic acid and purified by crystallisation from ethyl acetate–light petroleum, forming colourless needles, m. p. 200—201°, identical with an authentic specimen (Found : C, 60·9; H, 5·3. Calc. for $C_{12}H_{12}O_5$: C, 61·0; H, 5·1%).

Distillation of the aqueous liquors left on removal of the pyrousnic acid with the frequent addition of water so as to keep the volume constant gave an acidic aqueous distillate, which was neutralised with *N*-potassium hydroxide and evaporated. On the addition of acetone, a filtered alcoholic solution of the residue deposited characteristic crystals of potassium acetate, which was converted into silver salt (Found : Ag, 64·4. Calc. for $C_2H_3O_2Ag$: Ag, 64·7%).

(B) A solution of decarbousnic acid (2 g.) was heated with 60% aqueous potassium hydroxide (15 g.) at 90—100° in an atmosphere of hydrogen for ½ hour. On treatment with 2 : 4-dinitrophenylhydrazine hydrochloride in hydrochloric acid the small amount of aqueous distillate gave a precipitate of acetone-2 : 4-dinitrophenylhydrazone, which on purification had m. p. 128° and was identical with an authentic specimen.

The cooled reaction mixture was acidified with dilute sulphuric acid, and the precipitate of usnetic acid purified by means of aqueous sodium bicarbonate and then by crystallisation from dilute acetic acid, forming clusters of pale yellow needles, m. p. 210° (decomp.) after sintering at 188—191°, identical in every way with an authentic specimen, m. p. 211° (decomp.) with slight sintering at about 190°.

Usnolic Acid.—This compound was prepared from usnic acid (2·5 g.) according to the method of Widman (*Annalen*, 1902, **324**, 174) and after being separated from a little unchanged usnic acid was purified by crystallisation from alcohol, forming greenish-yellow laminæ (0·5 g.), m. p. 213—215° (decomp.) (compare Stenhouse and Grove, J., 1881, **39**, 234; Zopf, *Annalen*, 1900, **313**, 327; Widman, *loc. cit.*). When an intimate mixture of this acid (0·25 g.) and Kahlbaum's " Naturkupfer " (1 g.) was heated in a high vacuum at about 210—220°, decarbousnol sublimed; on recrystallisation from benzene it formed greenish-yellow laminæ, m. p. 204—205°. After sublimation in a high vacuum this material had m. p. 206° and was identified by comparison with a specimen of decarbousnol, m. p. 208°, prepared by Widman's method (*Annalen*, 1902, **324**, 184) (Found : C, 68·2; H, 5·5. Calc. for $C_{17}H_{16}O_5$: C, 68·0; H, 5·3%). The two compounds had the same crystalline form, solubilities, and ferric reaction (green, in alcohol) and on being mixed melted at 206—207°. Decarbousnol forms a yellow solution in sulphuric acid which on warming becomes red, brown-red and finally brownish-purple.

When a mixture of usnolic acid (0·4 g.) and aniline (1·5 c.c.) was heated on the water-bath for 1 minute, carbon dioxide was evolved and a crystalline product separated; this was collected, washed with a little warm alcohol, and recrystallised from acetic acid, forming slender needles, m. p. 231—232°, identical in every way with a specimen of the anil prepared from decarbousnic acid, m. p. 231—232° (Found : N, 3·4. Calc. for $C_{23}H_{23}O_5N$: N, 3·6%) (compare Widman, *Annalen*, 1902, **324**, 183, who gives m. p. 235—236°).

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