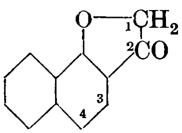
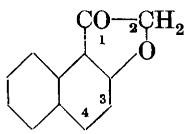
# CXXIX.—*Studies in the Coumaranone Series. Part III. Dihydro-α- and -β-naphthafuranones and their Condensation Products with Aromatic Aldehydes.*

By Bertram Hobart Ingham, Henry Stephen, and Ronald Timpe.

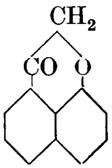
The method (Higginbotham and Stephen, J., 1920, **117**, 1534; Minton and Stephen, J., 1922, **121**, 1598) whereby the chlorides of aryloxyacetic acids are condensed in presence of aluminium chloride to give coumaranones has been applied to the chlorides of α- and β-naphthyloxyacetic acids. These give the corresponding dihydro-α- and -β-naphthafuranones, to which the structures (I) and (II) are assigned. The structure (III) for the substance named *dihydro-α-naphthafuran-2-one* cannot be ignored, however, since the benzylidene compound formed from it is not converted through the corresponding *dibromide* into a flavonol, which should be possible if it has the structure (I), but not if it has the structure (III). The latter structure (III) would also account for the difference in melting point and crystalline form between our product (needles, m. p. 119°) and the dihydro-α-naphthafuranone (thin laminæ, m. p. 91—92°) obtained by Ullmann (*Ber.*, 1897, **30**, 1468) from 1-hydroxy-2-naphthyl bromomethyl ketone. Structure (III) also receives support from the analogous condensation of α-naphthylacetyl chloride in presence of aluminium chloride to give acenaphthenone (D.R.-P. 230237); the formation of benzanthrone from α-benzoylnaphthalene in presence of aluminium chloride (Scholl, *Annalen*, 1912, **394**, 111) is a parallel example, and many similar instances of peri-ring closure are known.



(I.)



(II.)

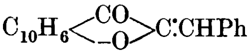


(III.)

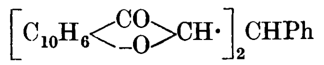
Our dihydro-β-naphthafuran-1-one (II) is identical with a specimen prepared by Fries and Frellstedt's method (*Ber.*, 1921, **54**, 715) from β-naphthyl chloroacetate by a reaction which involves the so-called Fries displacement: a mixture of the two showed no depression in melting point, and both substances gave 2-p-*dimethylaminoanilodihydro-*β*-naphthafuran-*1*-one* when condensed with *p*-nitrosodimethylaniline.

Both dihydronaphthafuranones (I) and (II) have been condensed with aromatic aldehydes, but the course of the reaction is determined by the nature of the condensing reagent. Benzaldehyde condenses with dihydro-α-naphthafuran-2-one in presence of hydrogen chloride, producing a mixture of *benzylidenedihydro-*α*-naphthafuran-*2*-one* (IV) and *benzylidenebis(dihydro-*α*-naphthafuran-*2*-one)* (V), of which the former is easily soluble in alcohol and the latter sparingly soluble: a similar difference in solubility is shown in other cases described in this communication. If acetic anhydride is employed to effect the condensation, (IV) is the only product obtained.

(IV.)



$$C_{10}H_6{<}{}^{CO}_{O}{>}C{:}CHPh$$



$$\left[C_{10}H_6{<}{}^{CO}_{O}{>}CH\cdot\right]_2CHPh$$

(V.)

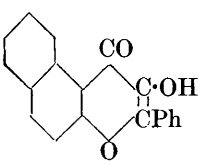
Condensation of dihydro-β-naphthafuran-1-one with benzaldehyde is most readily effected by acetic anhydride, the *benzylidene* compound similar to (IV) being the sole product. Hydrogen chloride gives only a very small yield of the same compound and no trace of a bis-compound similar to (V). Vanillin, on the other hand, condenses with dihydro-β-naphthafuran-1-one, in alcohol containing hydrogen chloride, to give 2-*vanillylidenedihydro-*β*-naphthafuran-*1*-one* and a small amount of the *bis-compound.* The latter is the chief product when vanillin is condensed in presence of hydrogen chloride with excess (2 mols.) of dihydro-β-naphthafuran-1-one. Acetic anhydride effects condensation of the same compounds, producing the *acetyl* derivative of vanillylidenedihydro-β-naphthafuran-1-one, from which on hydrolysis the latter is obtained. Ridgway and Robinson (J., 1924, **125**, 221) have shown that the sole product of the condensation of *o*-vanillin and dihydro-β-naphthafuran-1-one in alcoholic hydrogen chloride is *o*-vanillylidenedihydro-β-naphthafuran-1-one, but when a rapid stream of hydrogen chloride is passed through a solution of the compounds in acetic acid a pyrylium salt is produced.

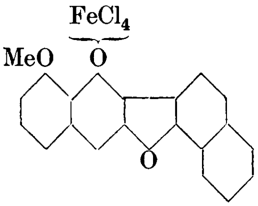
The condensation of dihydro-β-naphthafuran-1-one with piperonal by means of the same reagents gives results similar to those obtained with vanillin, but its condensation with *m*-hydroxybenzaldehyde gives only *m*-hydroxybenzylidenedihydro-β-naphthafuran-1-one.

The action of acetic anhydride on dihydro-α- and -β-naphthafuranones, which was studied prior to the use of the anhydride as a condensing agent, produces in each case the *acetyl* derivative of the corresponding enolic modification. This does not appear to have any appreciable effect on the condensations of aldehydes with the dihydronaphthafuranones. The latter both condense readily with *p*-nitrosodimethylaniline, giving 1-p-*dimethylaminoanilodihydro-α-naphthafuran-2-one* and the corresponding β-compound mentioned above: these derivatives are convenient for the identification of the dihydronaphthafuranones.

2-Benzylidenedihydro-β-naphthafuran-1-one reacts with bromine to give the corresponding *dibromide*, which is converted into 5 : 6-*benzflavonol* (VI) on treatment with aqueous potassium hydroxide. Considerable difficulty was experienced in preparing the dibromides of the other arylidene compounds described in this communication and the experiments were ultimately abandoned.

(VI.)





(VII.)

Ridgway and Robinson (*loc. cit.*) prepared 8-methoxy-β-naphthafurano-(2′ : 1′-2 : 3)-benzopyrylium ferrichloride by condensing dihydro-β-naphthafuran-1-one with *o*-vanillin. In a similar manner we have prepared *8-methoxy-α-naphthafurano-*(1′ : 2′-2 : 3)-*benzopyrylium ferrichloride* (VII) from dihydro-α-naphthafuran-2-one and *o*-vanillin.

## EXPERIMENTAL.

α-Naphthyloxyacetic acid was prepared by condensing chloroacetic acid with α-naphthol in alkaline solution (compare Spitzer, *Ber.*, 1901, **34**, 3191) and freed from α-naphthol by extraction with hot water, in which the α-acid (unlike the β-acid) is almost completely insoluble. The *acid chloride*, obtained from the acid by treatment with thionyl chloride, was a colourless oil, b. p. 194°/10 mm. (Found: Cl, 15·8. $C_{12}H_9O_2Cl$ requires Cl, 16·0%). Treated with aniline, it gave *α-naphthyloxyacetanilide*, which crystallised in colourless needles, m. p. 144°, from alcohol (Found: N, 5·0. $C_{18}H_{15}O_2N$ requires N, 5·1%).

*Dihydro-α-naphthafuran-2-one* (I).—The acid chloride (20 g.) was dissolved in 200 c.c. of benzene and maintained at 70° during the addition of aluminium chloride (16 g.), which required 6 hours. After remaining for 2 hours, the mixture was poured on ice and then submitted to steam-distillation. The product was slowly volatile in steam, and it was found desirable to extract the distillate with benzene. After several crystallisations from alcohol, it was obtained as pale yellow needles, m. p. 119°. It was readily soluble in acetic acid, acetone, benzene, chloroform, toluene, and hot alcohol. The solution in concentrated sulphuric acid was yellow with a green fluorescence. The compound slowly dissolved in aqueous sodium hydroxide, producing a pink coloration; with Fehling's solution, it developed a deep purple colour. It oxidised in the air, or when boiled with water, turning deep red (Found : C, 78·3; H, 4·6. $C_{12}H_8O_2$ requires C, 78·3; H, 4·4%). The *acetyl* derivative, prepared by boiling the above compound with acetic anhydride for an hour, crystallised from alcohol in reddish-brown needles, m. p. 85—86° (Found : C, 74·6; H, 4·8. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%).

1-p-*Dimethylaminoanilodihydro-α-naphthafuran-2-one* was obtained by treating *p*-nitrosodimethylaniline (1 mol.) with dihydro-α-naphthafuran-2-one in alcohol at 0° in presence of a trace of sodium hydroxide solution, and crystallised from alcohol–chloroform and then from alcohol, forming rectangular red plates, m. p. 210—211°, readily soluble in chloroform and sparingly in alcohol (Found : C, 75·4; H, 5·5. $C_{20}H_{16}O_2N_2$ requires C, 76·0; H, 5·1%). Its deep red solution in concentrated sulphuric acid became pale yellow on dilution with water.

1-*Benzylidenedihydro-α-naphthafuran-2-one* (IV).—A solution of benzaldehyde and dihydro-α-naphthafuran-2-one in acetic anhydride was warmed at 80° for ½ hour and poured into water. The *benzylidene* compound, which separated as a yellow mass, crystallised in golden-yellow needles, m. p. 130°, from alcohol. It gave a deep red coloration with concentrated sulphuric acid, was not affected by sodium hydroxide solution, and did not reduce Fehling's solution (Found : C, 83·75; H, 4·7. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%). The *dibromide*, prepared from the benzylidene compound and the requisite amount of bromine in chloroform, crystallised from alcohol–chloroform in pale yellow, prismatic needles, m. p. 198° (Found : Br, 37·1. $C_{19}H_{12}O_2Br_2$ requires Br, 37·0%).

*Benzylidenebis(dihydro-α-naphthafuran-2-one)* (V) was formed as a by-product when the condensation of benzaldehyde and dihydro-α-naphthafuran-2-one was carried out in alcoholic solution containing hydrogen chloride. It was readily separated from the above benzylidene compound by fractional crystallisation from alcohol, and obtained as cream-coloured rhombohedral plates, m. p. 197—198° (Found : C, 81·1; H, 5·0. $C_{31}H_{20}O_4$ requires C, 81·6; H, 4·4%).

β-*Naphthyloxyacetic Acid*.—This was prepared from β-naphthol and chloroacetic acid by Spitzer's method (*loc. cit.*), but it was found more convenient to purify the crude product from 80% alcohol. The *acid chloride* crystallised from benzene in needles, m. p. 54°, b. p. 207°/10 mm. (Found : Cl, 15·9. $C_{12}H_9O_2Cl$ requires Cl, 16·0%).

The *anilide* crystallised in colourless needles, m. p. 145° (Found: C, 77·7; H, 5·6. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4%).

*Dihydro-β-naphthafuran-1-one* (II).—This was prepared similarly to the α-compound, but was isolated by distillation with superheated steam owing to its slight volatility under ordinary conditions. It crystallised in colourless needles, m. p. 133°, soluble in the usual solvents (Found: C, 78·5; H, 4·6. Calc. for $C_{12}H_8O_2$: C, 78·3; H, 4·4%). Treated with concentrated sulphuric acid, it developed a purple coloration, and in aqueous sodium hydroxide it gave a green solution. Fehling's solution oxidised it, producing an intense purple compound. The *acetyl* compound crystallised in pale brown needles, m. p. 87—88° (Found: C, 74·1; H, 4·8. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%).

2-p-*Dimethylaminoanilodihydro-β-naphthafuran-1-one*, obtained in a similar way to the α-compound, crystallised from acetone in red needles, m. p. 231° when rapidly heated (Found: C, 76·0; H, 5·6. $C_{20}H_{16}O_2N_2$ requires C, 76·0; H, 5·1%). Its deep red solution in concentrated sulphuric acid became colourless on dilution with water.

2-*Benzylidenedihydro-β-naphthafuran-1-one* was readily obtained by boiling benzaldehyde and dihydro-β-naphthafuran-1-one in acetic anhydride for ½ hour. It crystallised in pale yellow needles, m. p. 150°, readily soluble in the usual solvents except ether and light petroleum. It gave an orange-coloured solution in concentrated sulphuric acid and was unaffected by aqueous sodium hydroxide and Fehling's solution (Found: C, 84·0; H, 4·6. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%). The *dibromide*, obtained by bromination of the benzylidene compound in chloroform solution, formed cream-coloured needles, m. p. 168° (Found: Br, 36·4. $C_{19}H_{12}O_2Br_2$ requires Br, 37·0%).

5 : 6-*Benzflavonol* (VI).—Potassium hydroxide (1·05 g.) in 150 c.c. of alcohol was gradually added to a boiling solution of the preceding dibromide (2 g.) in alcohol (100 c.c.), the colour of which changed from pale yellow to deep purple. After cooling, the solution was acidified, the alcohol removed by distillation, water added, and the precipitated *flavonol* removed by filtration. It crystallised from ethyl acetate in yellow needles, m. p. 147°, readily soluble in acetic acid and ethyl acetate and sparingly soluble in alcohol (Found: C, 79·6; H, 4·3. $C_{19}H_{12}O_3$ requires C, 79·2; H, 4·2%). The orange solution in concentrated sulphuric acid became pale blue on dilution with water and acquired a greenish fluorescence.

*Acetyl Derivative of 2-Vanillylidenedihydro-β-naphthafuran-1-one.*—This derivative, obtained by condensing vanillin with dihydro-β-naphthafuran-1-one in acetic anhydride solution, formed yellow needles, m. p. 178°, soluble in the usual solvents. It gave a deep red colour in concentrated sulphuric acid and a pink colour in aqueous sodium hydroxide and did not reduce Fehling's solution (Found : C, 73·6; H, 4·6. $C_{22}H_{16}O_5$ requires C, 73·3; H, 4·4%). On treatment with bromine in chloroform it gave the corresponding *dibromide* in colourless cubes, m. p. 200—201°, which produced an orange solution in concentrated sulphuric acid (Found : Br, 30·3. $C_{22}H_{16}O_5Br_2$ requires Br, 30·8%).

2-*Vanillylidenedihydro*-β-*naphthafuran*-1-*one* was obtained by hydrolysis of the acetyl derivative above in aqueous sodium hydroxide, and was precipitated from the alkaline solution on addition of hydrochloric acid. It was also obtained by saturating an alcoholic solution of vanillin (1 mol.) and dihydro-β-naphthafuran-1-one (1 mol.) with hydrogen chloride; after 1 hour, it crystallised in yellow needles. Recrystallisation from alcohol gave long yellow needles, m. p. 178°, soluble in the usual solvents, and in concentrated sulphuric acid with an orange-red coloration. Aqueous sodium hydroxide produced a faint crimson colour (Found : C, 75·8; H, 4·6. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%).

*Vanillylidenebis*(*dihydro*-β-*naphthafuran*-1-*one*) separated in almost quantitative yield when an alcoholic solution of dihydro-β-naphthafuran-1-one (2 mols.) and vanillin (1 mol.) was treated with gaseous hydrogen chloride. It crystallised from alcohol in pale orange-yellow needles, m. p. 223° (Found : C, 76·4; H, 4·6. $C_{32}H_{22}O_6$ requires C, 76·5; H, 4·4%).

*Piperonylidenedihydro*-β-*naphthafuran*-1-*one*, obtained by condensing piperonal (1 mol.) with dihydro-β-naphthafuran-1-one in presence of acetic anhydride, crystallised from benzene in yellow needles, m. p. 244°, very sparingly soluble in all the usual solvents. It gave a red solution in concentrated sulphuric acid (Found : C, 76·1; H, 4·0. $C_{20}H_{12}O_4$ requires C, 76·0; H, 3·8%).

*Piperonylidenebis*(*dihydro* - β - *naphthafuran* - 1 - *one*), prepared similarly to the vanillylidene compound, crystallised from benzene in yellow needles, m. p. 234—345°, sparingly soluble in the usual solvents. The solution in concentrated sulphuric acid was deep crimson (Found : C, 76·8; H, 4·2. $C_{32}H_{20}O_6$ requires C, 76·8; H, 4·0%).

8-*Methoxy*-α-*naphthafurano*-(1′ : 2′-2 : 3)-*benzopyrylium ferrichloride* (VII) was prepared at the suggestion of Professor R. Robinson by the method of Ridgway and Robinson (*loc. cit.*). It crystallised from much glacial acetic acid in small, dark red cubes, m. p. 230—231° (Found : C, 48·4; H, 3·0. $C_{20}H_{13}O_3Cl_4Fe$ requires C, 48·1; H, 2·6%).

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