

Studies on Lignin

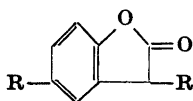
XVII.* Properties of Some 2'-Hydroxydesoxybenzoin

ÅKE SPETZ

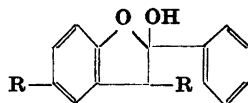
Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

As potential lignin models compounds of *semi-acetal* 2-phenylcoumaranol-(2) type (II) were desired. The reaction between coumaranone-(2) (Ia) and phenylmagnesium bromide yielded 3-(*o*-hydroxyphenylacetyl)-coumaranone-(2) (IV) — also obtained from coumaranone-(2) on treatment with potassium — and a small amount of 2'-hydroxydesoxybenzoin (IIIa) also obtained in good yield by reduction of *o*-hydroxybenzil. 3,5-Dimethylcoumaranone-(2) (Ib) and phenylmagnesium bromide gave exclusively $\alpha,5'$ -dimethyl-2'-hydroxydesoxybenzoin (IIIb). The 2'-hydroxydesoxybenzoin were readily dehydrated to the corresponding coumarones when treated with strong acids or subjected to a sulphite cook. Because of their instability it is unlikely that 2-phenylcoumaranol-(2) systems occur in lignin.

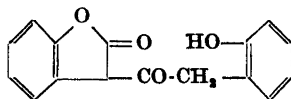
In connection with certain lignin chemical problems we were interested in the stability of compounds of the 2-phenylcoumaranol-(2) type (II)¹. A convenient method for the preparation of such compounds appeared to be the condensation of coumaranones with suitable phenylmagnesium halides.



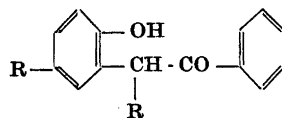
Ia R = H
Ib R = CH₃



IIa R = H
IIb R = CH₃



IV



IIIa R = H
IIIb R = CH₃

* Part XVI. *Svensk Papperstidn.* 55 (1952) 816.

When an ethereal solution of phenylmagnesium bromide was added to coumaranone, $C_8H_6O_2$ (Ia), reaction took place but from the reaction product only a small amount of a substance, $C_{14}H_{12}O_2$ (A), could be isolated. The main product was a pale yellow compound, $C_{16}H_{12}O_4$.

It was suspected that the latter compound might be 3-(*o*-hydroxyphenylacetyl)-coumaranone-(2) (IV) formed by an acetoacetic ester type of condensation from two molecules of coumaranone, the Grignard reagent simply functioning as the base catalyst. The correctness of this assumption was shown by the formation of the same compound when a solution of coumaranone in dry ether was treated with potassium.

Compound A could be more conveniently obtained by reduction of *o*-hydroxybenzil with zinc in the presence of ammonium chloride (compare Pearl² for the similar reduction of vanillil to desoxyvanilloin).

3,5-Dimethylcoumaranone-(2) (Ib) was prepared by transforming 2-methoxy-5-methylacetophenone into its cyanohydrin which was hydrolysed to 2-methoxy-5-methylhydratropic acid. The acid was demethylated with pyridinium chloride and distilled to give the desired product. This compound when treated with phenylmagnesium bromide furnished a compound, $C_{16}H_{16}O_2$ (B), in moderate yield. No condensation products of the acetoacetic ester type could be isolated in this case.

Compound A is not the semiacetal 2-phenylcoumaranol-(2) (IIa) but the corresponding 2'-hydroxydesoxybenzoin (IIIa) and compound B is $\alpha,5'$ -dimethyl-2'-hydroxydesoxybenzoin (IIIb). This follows from the close similarity of the U.V. absorptions of compound A, its methyl ether, compound B and desoxybenzoin³.

	Maxima:	$m\mu$	$\log \epsilon$	$m\mu$	$\log \epsilon$
Desoxybenzoin		240	4.10	278*	2.90
2'-Methoxydesoxybenzoin		243	4.03	275*	3.42
2'-Hydroxydesoxybenzoin (comp. A)		242	4.13	275*	3.54
$\alpha,5'$ -Dimethyl-2'-hydroxydesoxybenzoin (comp. B)		245	4.11	283	3.50

* inflexion

In 0.25 N sodium hydroxide solution the phenol-phenolate shift was observed with compound A (max.: 240 $m\mu$, $\log \epsilon$ 4.29; infl.: 288 $m\mu$, $\log \epsilon$ 3.70). However, above 350 $m\mu$ a new maximum was gradually developed ($\log \epsilon$ increasing from 2.7 to 3.3 at 400 $m\mu$ in 90 minutes). This indicates that some secondary changes take place. Moreover the original absorption was not immediately restored on acidification.

When compound A was treated with acids, water was easily eliminated and 2-phenylcoumarone was formed and similarly when heated with bisulphite cooking acid 2-phenylcoumarone was obtained but no sulphonic acid.

Compound B behaved in exactly the same manner yielding 3,5-dimethyl-2-phenylcoumarone in good yield.

These results indicate that it is unlikely that 2-hydroxy-2-phenylcoumarone systems occur in lignin.

EXPERIMENTAL *

2'-Hydroxydesoxybenzoin (IIIa). Method a. Phenylmagnesium bromide (from 7.8 g bromobenzene) in dry ether (100 ml) was slowly added with mechanical stirring to coumaranone-(2) (10 g) in dry ether (50 ml). The reaction product was decomposed with ammonium chloride in ice-water and the aqueous phase carefully acidified with dilute hydrochloric acid (to pH 2–3) and extracted with ether. The combined ether solutions were washed with cold dilute hydrochloric acid and then extracted with dilute sodium hydroxide. Carbon dioxide was bubbled into the alkaline solution and at pH 9 a pale yellow precipitate formed which was dissolved in ether. The ether solution was dried over magnesium sulphate and evaporated to dryness. The residue (compound A, 1.5 g) was crystallised from ethanol-water. Pale yellow crystals starting to sinter at 110° and, melting at about 120°. The unsharp melting point is probably due to loss of water and partial formation of 2-phenylcoumarone. (Found: C 80.5; H 5.6. Calc. for $C_{14}H_{12}O_2$: C 79.2; H 5.7).

Method b. *o*-Hydroxybenzil (1.6 g) in ethanol (100 ml) and zinc dust (5 g) were heated to boiling and a warm solution of ammonium chloride (5 g) in water (20 ml) added and the mixture boiled under reflux for one hour. The zinc was removed and acetic acid (10 ml) carefully added to the cooled solution which was then concentrated at reduced pressure to a small volume whereupon water (100 ml) was added. The remaining ethanol was now removed by further distillation. On cooling a pale yellow precipitate was obtained. The product (0.9 g) was dissolved in dilute aqueous alkali, filtered and precipitated with carbon dioxide. Crystallisation from ethanol-water gave crystals m.p. 110–120° (decomp.).

2'-Methoxydesoxybenzoin, which is a stable compound with a sharp melting point, was prepared in order to identify the reaction products from *methods a* and *b* by dissolving 2'-hydroxydesoxybenzoin (0.5 g), prepared according to either of the methods, in 2 N aqueous sodium hydroxide (5 ml) and shaking with dimethyl sulphate (0.5 ml). The crystalline reaction product was dissolved in ether and the solution filtered through a short column of aluminium oxide. On evaporation almost pure methyl ether m.p. 59–60° was obtained. Recrystallisation from a small volume of methanol raised the m.p. to 61.5–62°. The products obtained from both preparations were identical (mixed m.p.). (Found: C 79.7; H 6.4; OCH_3 13.6. Calc. for $C_{15}H_{14}O_2$: C 79.6; H 6.2; OCH_3 13.7).

3-(o-Hydroxyphenylacetyl)-coumaranone-(2) (IV). Method 1. On further acidification of the alkaline phase from the preparation of 2'-hydroxydesoxybenzoin according to *method a* (to pH 6–7) a precipitate (3.5 g) was obtained. Crystallisation from ethanol-water yielded pale yellow needles m.p. 150–155° (decomp.) (Found: C 71.5; H 4.7. Calc. for $C_{16}H_{12}O_4$: C 71.6; H 4.5).

Method 2. In a flask fitted with a condenser, potassium (1.2 g) was powdered under dry toluene (100 ml) which was then replaced by dry ether (25 ml). Coumaranone-(2) (4.6 g) in dry ether (50 ml) was added through the condenser with shaking at room temperature. The mixture was then boiled for six hours and left overnight. Acetic acid (2.5 ml) in water (25 ml) was added with vigorous shaking. The ethereal layer was separated, washed with water, dried over magnesium sulphate and evaporated to dryness. Crystallisation of the residue (2 g) from ethanol-water yielded a pale yellow substance m.p. 151–154° not depressed on admixture with 3-(*o*-hydroxyphenylacetyl)-coumaranone-(2) from the previous experiment (*method 1*).

2-Phenylcoumarone. 2'-Hydroxydesoxybenzoin (0.5 g) was dissolved in acetic acid (2 ml) and conc. hydrochloric acid (2 drops) added. On heating the solution to boiling it gave almost instantly a white precipitate. It was collected, dissolved in ether, shaken with dilute aqueous alkali, dried over calcium chloride and the solution evaporated to dryness. Crystallisation of the residue (0.4 g) from ethanol gave white plates exhibiting a blue fluorescence, m.p. 120.5–121°. (Found: C 86.4; H 5.2. Required for $C_{14}H_{10}O$: C 86.6; H 5.2).

2-Methoxy-5-methylhydratropic acid. Concentrated hydrochloric acid (70 ml, *d* 1.18) was added from a dropping funnel in five to ten drop portions to a mixture of 2-methoxy-5-methylacetophenone (82 g) and potassium cyanide (55 g) and ether (100 ml) cooled in

* All melting points uncorrected.

ice-water and vigorously stirred. The pale yellow colour appearing at each addition of the acid was allowed to disappear before the next addition. Towards the end of the reaction the mixture remained yellow. The ethereal layer was separated, washed several times with water, concentrated at reduced pressure and the crude 2-methoxy-5-methylacetophenone cyanohydrin (100 g) used for the next step without further purification.

Crystalline stannous chloride (100 g), acetic acid (100 ml), conc. hydrochloric acid (100 ml) and hydriodic acid (10 ml, d 1.7) were added to the crude 2-methoxy-5-methylacetophenone cyanohydrin (100 g). The mixture was heated on a steam bath for five hours. After cooling the mixture was filtered and the filtrate diluted with water and extracted with ether. The ethereal solution was extracted with sodium bicarbonate solution from which on acidification with hydrochloric acid a colourless crystalline product (18 g) was precipitated. The substance crystallised from ethanol-water in plates, m.p. 125–126°. (Found: C 68.5; H 7.3; Equiv. wt. 192. Calc. for $C_{11}H_{14}O_3$: C 68.0; H 7.3; Equiv. wt. 194).

The ethereal solution was then extracted with 2 N sodium hydroxide from which on acidification a crystalline, phenolic substance (about 5 g) was obtained by extraction with ether. The substance crystallised from ligroin in needles m.p. 47–48° undepressed on admixture with 2-hydroxy-5-methylacetophenone. It is evidently formed by demethylation of unchanged 2-methoxy-5-methylacetophenone.

The amide of 2-methoxy-5-methylhydratropic acid separated from the aqueous phase on standing and was crystallised from benzene. Plates, m.p. 144–145°. (Found: N 7.25. Calc. for $C_{11}H_{15}O_2N$: N 7.25). It was converted to 2-methoxy-5-methylhydratropic acid, m.p. 125–126° undepressed on admixture with an authentic specimen, by refluxing with 50 % ethanolic potassium hydroxide for five hours.

Concentration of the extracted solution yielded a residue (about 40 g) consisting chiefly of unchanged 2-methoxy-5-methylacetophenone.

3,5-Dimethylcoumaranone-(2) (Ib). A mixture of 2-methoxy-5-methylhydratropic acid (17 g) and pyridinium chloride (50 g) was heated to 180° for two hours. The reaction mixture was poured into 2 N hydrochloric acid (500 ml) and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid and with water. After removal of the ether and distillation of the residual oil at reduced pressure a colourless product (12 g) was obtained which readily crystallised. Plates, m.p. 36–37°. Crystallisation from methanol-water and repeated distillation raised the melting point to 39–39.5°. (Found: C 74.3; H 6.5. Calc. for $C_{10}H_{10}O_2$: C 74.1; H 6.2).

a,5'-Dimethyl-2'-hydroxydesoxybenzoin (IIIb). Phenylmagnesium bromide (from 3.1 g bromobenzene) in dry ether (10 ml) was slowly added to a solution of 3,5-dimethylcoumaranone-(2) (4 g) in dry ether (150 ml) with mechanical stirring. The reaction product was worked up exactly in the same way as for 2'-hydroxydesoxybenzoin and yielded a crystalline substance (1.5 g) melting at 125–127°. Recrystallisation from ligroin gave needles m.p. 129.5–130°. (Found: C 80.1; H 6.8. Calc. for $C_{16}H_{16}O_2$: C 80.0; H 6.7).

Sulphite cooking of the desoxybenzoin. The cooking acid was obtained by bubbling sulphur dioxide into 10 % aqueous sodium hydroxide until the desired pH was reached. The heating was carried out in a sealed glass tube. Time 12 hours. Temperature 135°C.

2'-Hydroxydesoxybenzoin. a: pH 1.5. The compound (0.5 g) was heated with cooking acid (10 ml). The reaction mixture was extracted with ether which was then washed with dilute alkali, dried over calcium chloride and concentrated. A crystalline substance (0.5 g) m.p. 118–120° with a blue fluorescence was obtained. Recrystallisation from ethanol yielded plates, m.p. 120–121° showing no depression when mixed with 2-phenylcoumarone. *b:* pH 5.5. The experiment was carried out in a similar way and the alkali-washed ethereal solution on concentration yielded 2-phenylcoumarone (0.4 g). When carbon dioxide was bubbled through the alkaline washings unchanged 2'-hydroxydesoxybenzoin (0.1 g) was recovered.

a,5'-Dimethyl-2'-hydroxydesoxybenzoin. The experiments were carried out as above. At pH 1.4 3,5-dimethyl-2-phenylcoumarone was obtained in a quantitative yield. Crystallisation from methanol gave needles exhibiting a strong blue fluorescence m.p. 69.5–70° (Found: C 86.7; H 6.2. Calc. for $C_{16}H_{14}O$: C 86.5; H 6.3).

No sulphonic acids were found in any of these experiments.

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