XCV.—*The Absorption Spectra of Phloroglucinol and some of its Derivatives.*

By W. N. HARTLEY, D.Sc., F.R.S., JAMES J. DOBBIE, D.Sc., M.A., and
ALEXANDER LAUDER, B.Sc.

PHLOROGLUCINOL reacts with some reagents as a phenol, with others as a ketone. When heated with phenyl isocyanate in benzene solution, it yields a tricarbanilide derivative, $C_6H_3(O \cdot CO \cdot NHC_6H_5)_3$, and when alkylated under certain conditions it gives derivatives which are regarded as true esters since their alkyl groups are split off by heating with hydrogen iodide. On the other hand, it reacts with hydroxylamine with the formation of a trioxime, and forms alkylated derivatives from which the alkyl groups are not split off by boiling with hydrogen iodide. It is impossible, therefore, from its chemical behaviour to decide whether the oxygen atoms of phloroglucinol are present in enolic or ketonic groups, that is to say, whether it possesses the structure (I) or (II) :

Enolic.

Ketonic.

If it possesses the structure represented by I, its absorption spectra

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should closely resemble the spectra of the trimethyl ether (m. p. 52°) which is decomposed by boiling with hydrogen iodide. If, on the other hand, it possesses the structure represented by II, its spectra should resemble those of the alkyl derivatives which are not decomposed under this treatment.

Before comparing the absorption spectra of phloroglucinol with those of its ethers, we deemed it advisable to examine specimens of phloroglucinol from as many different sources as possible, and for this purpose specimens were prepared from kino, maclurin, resorcinol, phenol, and ethyl phloroglucinoltricarboxylate.

As the melting point of phloroglucinol is variously stated at temperatures ranging from 210° to 217° , we made a careful comparison of all our pure preparations with the view of determining whether specimens prepared from different sources really differ from one another as regards this property or whether the differences observed are merely due to the various determinations not having been made under the same conditions (compare Baeyer, *Ber.*, 1886, 19, 2186).

We first compared several specimens of phloroglucinol from kino which had been carefully purified by recrystallisation and found that when slowly heated side by side they melted at 210° and when quickly heated at 217° .

All the other specimens when heated side by side with the specimen from kino behaved in the same way.

The absorption spectra of aqueous solutions of all the five specimens were photographed, and on comparison were found to be practically identical.

It may therefore be regarded as definitely established that phloroglucinol, from whatever source obtained, has always the same structure.

On next comparing the spectra of phloroglucinol with those of the trimethyl ether (m. p. 52°), the resemblance between them was found to be so close as to leave no doubt as to the enolic structure of phloroglucinol, assuming that the alkyl derivative melting at 52° possesses this structure.

Further, the resemblance is so close that it is impossible to suppose that the phloroglucinol contains any appreciable quantity of a ketonic form.

Both phloroglucinol and its trimethyl ether show selective absorption, the absorption band, however, not being strongly marked. If phloroglucinol possessed the ketonic structure, we should expect the absorption band to be entirely absent, since diketohexamethylene, formula III, a substance of similar structure to the ketonic derivatives

of phloroglucinol, shows only general absorption (Trans., 1898, 73, 598).

On the other hand, the presence of an absorption band is characteristic of substances having the true benzenoid structure which phloroglucinol, if represented by formula I would possess.

We prepared hexamethylphloroglucinol by the method given by Margulies (*Monatsh.*, 1888, 9, 1046). The product which we obtained had the correct melting point (80°), and agreed generally in properties with the substance described by Margulies. We found, however, that specimens of the substance crystallised from ether and from acetic acid, although having the same melting point, did not give identical absorption spectra. We therefore omit any detailed account of this substance until we have had an opportunity of investigating it more fully. We may mention, however, that none of the absorption spectra observed in different solutions of this substance at all resembled those of phloroglucinol.*

Confirmation of the conclusion arrived at as to the structure of phloroglucinol is afforded by the great similarity which exists between the spectra of phloroglucinol and those of pyrogallol, a substance which does not show the behaviour of a ketone (Baeyer, *Ber.*, 1886, 19, 163). The spectra of pyrogallol have already been described by Hartley and Huntington (*Phil. Trans.*, 1879, i, 257), but as the method of representation employed at that time was different from that now adopted, we have rephotographed the spectra and drawn a new curve to facilitate comparison with phloroglucinol.

For the same reason, we include in this paper an account of the re-examination of the absorption spectra of phenol (Hartley and Huntington, *loc. cit.*). We have also photographed and remeasured the absorption spectra of quinol, resorcinol, and catechol, which were described by Hartley in 1888 (Trans., 1888, 53, 641).

The new and old series of measurements being in close agreement, we have not thought it necessary to repeat them in this paper.

On comparing the mono-, di-, and tri-hydroxy-derivatives, it will be observed that whilst the spectra of the mono- and di-derivatives agree very closely, those of phenol and catechol being almost identical, the spectra of the trihydroxy-derivatives differ from the others in showing

* It is worthy of note that hexamethylphloroglucinol does not form a compound with phenylhydrazine.

less general absorption and in having the absorption band much less distinctly marked.

EXPERIMENTAL.

Phloroglucinol.—The specimens of phloroglucinol which we examined were obtained from five different sources.

(1) Specimens prepared from kino were obtained from Merck and from Schuchardt. Both preparations were supplied to us in beautiful, scaly crystals which were practically colourless, and behaved in exactly the same way when heated side by side. They were recrystallised repeatedly from water before being photographed.

(2) Commercial phloroglucinol, prepared by Schuchardt from resorcinol, was purified by the method given by Will (*Ber.*, 1885, 18, 1323) and Skraup (*Monatsh.*, 1889, 10, 724). The purification was completed by boiling the substance with charcoal and crystallising it repeatedly from water. The specimen was then tested for diresorcin by dissolving it in concentrated sulphuric acid and heating the solution on the water-bath with acetic anhydride. No violet coloration was produced (Herzig and Zeisel, *Monatsh.*, 1890, 11, 421). All the specimens of commercial phloroglucinol used in the course of the investigation were purified by the above method.

(3) Phloroglucinol was prepared from the tricarboxylic ester by fusion with potassium hydroxide (Baeyer, *Ber.*, 1886, 18, 3454). The specimen obtained by this method crystallised very readily in beautiful scales, which, after being recrystallised several times, had the correct melting point.

(4) The method given by Barth and Schreder (*Ber.*, 1879, 12, 417) was employed in the preparation of a fourth specimen. Phenol was melted with six times its weight of sodium hydroxide and heated until the evolution of hydrogen ceased. The fused mass was acidified with dilute sulphuric acid and the phloroglucinol extracted with ether. The yield of phloroglucinol was small. So far as we could discover, its properties were identical with those of the other specimens which we examined. It melted at the same temperature as the specimens from kino when the determinations were carried out side by side. Its absorption spectra were also identical with those of the specimens from kino. If, as stated by Gautier (*Bull. Soc. Chim.*, 1880, [ii], 33, 585), an isomeride of phloroglucinol is obtained by fusing phenol with soda, it is certain that phloroglucinol is likewise one of the products of the reaction.

(5) A fifth specimen was prepared from maclurin by fusion with potassium hydroxide according to the method described by Hlasiwetz and Pfaundler (*Annalen*, 1863, 127, 351).

The absorption spectra of the aqueous solutions of all the specimens

of phloroglucinol described above were photographed, and, on comparison, found to be identical. The measurements were actually taken and the curve drawn from the photographs of the specimen prepared from resorcinol and purified by Skraup's method.

A layer 50 mm. thick of a solution containing 1 milligram-mol. in 20 c.c. of water absorbs all rays beyond $1/\lambda$ 3323 ($\lambda = 3009$), whilst a layer 5 mm. thick of the same solution absorbs all rays beyond $1/\lambda$ 3568 ($\lambda = 2802$).

The absorption band is not strongly marked ; it appears first in the layer 3 mm. thick of the solution containing 1 milligram-mol. in 100 c.c. water, and nearly dies out in the layer 2 mm. thick of the same solution, although its position is still distinctly traceable by the weakness of the spectra in solutions of greater dilution.

The absorption spectra of phloroglucinol in both aqueous and in alcoholic solutions are identical.

Phloroglucinol Trimethyl Ether.—This ether was prepared by saturating a solution of pure phloroglucinol in methyl alcohol with hydrochloric acid gas, and subsequently treating the dimethyl ether so obtained with methyl iodide and potassium hydroxide dissolved in methyl alcohol (Will, *Ber.*, 1888, 21, 603). The product is an oil which quickly solidifies to beautiful, colourless prisms, melting at 52.5° .

The spectra of this substance in alcoholic solution were photographed and the ether was afterwards recovered from the alcoholic solution and found to be unaltered. The spectra are practically identical with those of phloroglucinol, as will be seen from a comparison of the measurements and curves.

Pyrogallol.—A specimen of pyrogallol obtained from Schuchardt was purified by recrystallisation. It melted at $132-134^\circ$. It was photographed in aqueous solution, and gave spectra very similar to those of phloroglucinol. The amount of general absorption is slightly greater, and the absorption band, which occupies the same position, is somewhat narrower, but dies out at the same degree of dilution as in the case of phloroglucinol.

Phenol.—The specimen employed was prepared from pure salicylic acid by distillation with lime. It boiled at 182° .

Phloroglucinol, $C_6H_3(OH)_3$ [1:3:5].

Prepared from resorcinol and purified by Skraup's method.

M. p. 210—217°.

Thickness of layer of liquid in mm.	Description of spectrum.	$1/\lambda$.	λ .
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1 milligram-mol. in 20 c.c. water.

50 and 25	Spectrum continuous to	3323	3009
20 and 15	„ „	3362	2974
10	„ „	3521	2840
5, 4, 3, 2	„ „	3568	2802

1 milligram-mol. in 100 c.c. water.

5	Spectrum continuous to	3638	2748
	Absorption band	3638—3886	2748—2573
	Line at	3886	2573
	Very faint indication of spectrum beyond this.		
4 and 3	Same as 5 mm.		
2	Spectrum continuous to	3638	2748
	Absorption band	3638—3886	2748—2573
	Line showing in absorption band at ...	3693	2707
	and	3824	2615
	Weak spectrum.....	3886—4133	2573—2419
1	Spectrum practically continuous to ...	4133	2419
	Still weak in the position of the absorption band.		

1 milligram-mol. in 500 c.c. water.

5	Spectrum practically continuous to ...	4133	2419
	But still weak in the position of the absorption band.		
4 and 3	Spectrum continuous to	4175	2395
2	„ „	4320	2314
1	„ „	4421	2261

Phloroglucinol Trimethyl Ether, $C_6H_3(O\cdot CH_3)_3$. M. p. 52.5°.

Thickness of layer of liquid in mm.	Description of spectrum.	$1/\lambda$.	λ .
<i>1 milligram-mol. in 100 c.c. alcohol.</i>			
25	Spectrum continuous to	3534	2829
20 } 15 } 10 } 5 }	" "	3568	2802
	" "	3638	2748
	Absorption band	3638—3886	2748—2573
	Line at	3886	2573
4	The same as 5.		
3	Spectrum continuous to	3638	2748
	Absorption band	3638—3886	2748—2573
	Lines showing in absorption band at ...	3694	2707
	and	3824	2615
	Very faint indications of spectrum beyond	3886	2573
2	Spectrum practically continuous to ...	4038	2476
1	Still weak in position of band.		
	Spectrum continuous to	4133	2419
<i>1 milligram-mol. in 500 c.c. alcohol.</i>			
5, 4, 3, 2	Spectrum continuous to	4133	2419
1	" "	4421	2261

Pyrogallol, $C_6H_3(OH)_3$ [1 : 2 : 3]. M. p. 132—134°.

Thickness of layer of liquid in mm.	Description of spectrum.	$1/\lambda$.	λ .
<i>1 milligram-mol. in 20 c.c. water.</i>			
25	Spectrum continuous to	3385	2954
20 } 15 } 10 }	" "	3474	2878
	" "	3491	2864
5 } 4 } 3 } 2 } 1 }	" "	3521	2840

Scale of oscillation frequencies.

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Pyrogallol, $C_6H_3(OH)_3$ [1 : 2 : 3]. M. p. 132—134° (*continued*).

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ .
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1 milligram-mol. in 100 c.c. water.

5 and 4	Spectrum continuous to	3568	2802
3	" "	3638	2748
2	" "	3638	2748
	Absorption band	3638—3824	2748—2615
	Lines showing in band at ..	3694	2707
	Very weak spectrum.....	3824—4125	2707—2424
1	Spectrum practically continuous to ...	4125	2424
	Still weak in position of the absorption band.		

1 milligram-mol. in 500 c.c. water.

5	Spectrum practically continuous to ... But still weak in position of absorption band.	4125	2424
4	Spectrum continuous to	4165	2400
	Still weak in absorption band.		
3	Spectrum continuous to	4297	2327
2	" "	4321	2314
1	" "	4405	2270

Phenol, $C_6H_5 \cdot OH$. B. p. 182°.

Thickness of layer of liquid in mm.	Description of spectrum.	$1/\lambda$.	λ .
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1 milligram-mol. in 20 c.c. alcohol.

25 and 20	Spectrum continuous to	3179	3145
15	" "	3179	3145
	Faint prolongation to	3240	3086
10 and 5	Spectrum continuous to	3295	3034
4 and 3	" "	3323	3009
2	" "	3354	2981
1	" "	3429	2916
	Lines showing very faintly at.....	4112	2431
		4125	2424
	and	4245	2355

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Phenol, $C_6H_5 \cdot OH$. B. p. 182° (continued).

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$.	λ .
<i>1 milligram-mol. in 100 c.c. alcohol.</i>			
5	Spectrum continuous to Lines showing as in (1) above.	3429	2916
4	Spectrum continuous to Absorption band Spectrum	3429 3429—4112 4112—4125	2916 2916—2431 2431—2424
3	Spectrum continuous to Absorption band Spectrum continuous	3491 3491—4112 4112—4245	2864 2864—2431 2431—2355
2	Spectrum continuous to Absorption band Spectrum continuous	3521 3521—3886 3886—4321	2840 2840—2573 2573—2314
1	Spectrum continuous to Absorption band Spectrum continuous	3527 3527—3824 3824—4321	2835 2835—2615 2615—2314
<i>1 milligram-mol. in 500 c.c. alcohol.</i>			
5	Same as (1) above.		
4	Spectrum continuous to Absorption band Spectrum continuous	3527 3527—3824 3824—4368	2835 2835—2615 2615—2289
	Lines showing in absorption band at... and	3568 3638	2802 2748
3	Spectrum practically continuous to ... But still very weak in the position of the absorption band.	4368	2289
2 and 1	Spectrum continuous to	4413	2266