XLII.—*On the Hydride of Butyro-salicyl and Butyric Coumaric Acid.*

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IN a previous communication* it has been shown that in the formation of coumarin, by means of acetic anhydride and hydride of sodium-salicyl, the first product of the reaction is the hydride of aceto-salicyl, and that this body is subsequently transformed into coumarin by the separation of a molecule of water. Having obtained homologues of coumarin by substituting other anhydrides for the acetic, it appeared desirable to follow up the changes which take place in the formation of one of these new products, and at the same time to further establish its relationship to ordinary coumarin by the production of a new coumaric acid. I have therefore investigated the changes which take place in the formation of butyric coumarin and its corresponding acid.

Hydride of Butyro-salicyl.

A solution of butyric anhydride in anhydrous ether is left in contact with hydride of sodium-salicyl for two or three days, the reagents being used in equivalent quantities. The ethereal solution is then filtered off from the butyrate of sodium formed, and agitated with a small quantity of a dilute solution of carbonate of sodium. It is then dried over anhydrous carbonate of sodium and distilled. After the ether has passed over, the temperature gradually rises, but no very steady boiling point is observed; the principal product however comes over at about 260°—270° C., and is collected apart. Three combustions of this body gave the following numbers:—

- I. ·1925 of substance gave
·4835 of CO₂, and
·1096 of H₂O.
- II. ·2002 of substance gave
·5026 of CO₂, and
·1116 of H₂O.

* Vol. vi, p. 181.

III. ·2508 of substance gave
 ·6289 of CO_2 , and
 ·1392 of H_2O .

These results give percentages agreeing with the formula,

as the following comparisons show :—

	Theory.		Experiment.		
			I.	II.	III.
C_{11}	132	68·75	68·50	68·46	68·38
H_{12}	12	6·25	6·32	6·19	6·16
O_3	48	25·00	—	—	—
	<hr/>	<hr/>			
	192	100·00			

The product therefore represents the hydride of salicyl, with an equivalent of hydrogen replaced by butyryl, its formation being analogous to that of the hydride of aceto-salicyl.

The hydride of butyro-salicyl is an oil boiling at about 260° — 270° C. It has a slightly butyric odour mixed with that of the hydride of salicyl. It is soluble in all proportions in alcohol and ether.

With bisulphite it appears to decompose into butyric acid and hydride of salicyl, the latter combining with the bisulphite.

A strong solution of hydrate of potassium decomposes it immediately, forming a solid mass of the hydride of potassium-salicyl and butyrate of potassium; this decomposition is attended with a considerable elevation of temperature.

Acetic Anhydride and Hydride of Butyro-salicyl

A mixture of the hydride of butyro-salicyl and acetic anhydride, when heated in a sealed tube to 140° or 150° C. for a few hours, becomes slightly brown. On opening the tube and leaving the product in contact with water for a day or two,

crystals separate; these, when pressed between bibulous paper, and twice crystallised from alcohol, gave the following numbers on analysis :—

·2094 of substance gave—
 ·4524 of C_2O_2 ,
 ·1057 of H_2O .

These results give numbers corresponding with those required by the formula

as the following comparisons will show :—

	Theory.		Experiment.
C_{13}	156	58·64	58·92
H_{14}	14	5·26	5·60
O_6	96	36·10	—
	<hr/> 266	<hr/> 100·00	

This formula is that of the compound of the hydride of aceto-salicyl and acetic anhydride. Its identity was confirmed by the determination of its melting point.

In the formation of this product the radical butyryl has been replaced by acetyl, a mixed anhydride being probably formed at the same time, thus—

Formation of Butyric Coumarin from Hydride of Butyro-salicyl.

Hydride of butyro-salicyl when distilled alone does not appear to yield a coumarin, but if boiled with a mixture of butyric anhydride and butyrate of sodium for a short time, washed from saline matter with water, and then distilled, the last third of the distillate will be found to solidify on cooling. This solid product, when separated from oily matter by pressure between bibulous paper and then crystallised from alcohol, is

found to be pure butyric coumarin, possessing the correct melting point and characteristic odour.

The formation of this body is therefore perfectly analogous to that of ordinary coumarin.

Butyric Coumaric Acid.

Butyric coumarin dissolves in boiling aqueous hydrate of potassium. Upon evaporating this solution, an oily layer forms, and if the liquid be then allowed to cool, this oily compound becomes a hard, tenacious mass, from which the alkaline solution may be easily decanted. This product is apparently a compound of one molecule of coumarin with one of hydrate of potassium, and is therefore isomeric with the potassium salt of a butyric coumaric acid. On heating this body in a dish, it fuses and boils up; it then becomes more pasty and frothy, and soon breaks up into soft masses.

This fused product is perfectly soluble in water, and on the addition of hydrochloric acid to its solution, it becomes a pure white mass of minute crystals. To separate any unchanged butyric coumarin from this product, it was dissolved in a little ammonia, filtered, thrown down with acid, washed well with water, and dried. Thus obtained it still contains a small quantity of butyric coumarin. This is easily separated by digestion with chloroform, in which the new body is very difficultly soluble. It is then further purified by crystallisation from dilute alcohol. A combustion of a specimen dried at 100° C. gave the following numbers :—

·1819 of substance gave—
·4556 of CO₂, and
·1058 of H₂O.

These numbers give percentages agreeing with the formula—

as the following comparisons will show :—

	Theory.		Experiment.
C ₁₁	132	68·75	68·30
H ₁₂	12	6·25	6·46
O ₃	48	25·00	—
	<hr/> 192	<hr/> 100·00	

This product is evidently butyric coumaric acid, the third of the series.

$C_9H_8O_3$ coumaric acid.

$C_{10}H_{10}O_3$ propionic coumaric acid (not known).

$C_{11}H_{12}O_3$ butyric coumaric acid.

It is also isomeric with the hydride of butyro-salicyl.

Butyric coumaric acid crystallises in flat prisms, having a brilliant lustre. It fuses at about $174^\circ C.$, but undergoes slight decomposition at that temperature. It is extremely soluble in alcohol and ether, but difficultly so in water and chloroform. It does not colour the solutions of the persalts of iron. It is but feebly acid in its characters, but will decompose a boiling solution of carbonate of sodium with effervescence.

Like ordinary coumaric acid, it forms only monometallic derivatives.

Sodium salt.—This body is prepared by boiling the acid with a solution of carbonate of sodium, keeping the acid in excess. The solution is then allowed to stand for a day, filtered, and evaporated. It is a crystalline and very soluble salt.

Silver salt.—A solution of the sodium salt gives a pale yellow precipitate with nitrate of silver; this, however, suddenly changes, becoming nearly white and crystalline. It is slightly soluble in water, and also in the above sodium salt. It requires careful drying for analysis, as it is apt to blacken at $100^\circ C.$, whilst a lower temperature does not appear to be sufficient for its complete desiccation. It gave the following results upon analysis:—

- I. 0.2012 of substance gave—
 - 0.3235 of CO_2 ,
 - 0.0706 of H_2O , and
 - 0.0733 of Ag.
- II. 0.1338 of substance gave—
 - 0.0480 of Ag.

These numbers give percentages agreeing with the formula—

as the following comparisons will show:—

		Theory.		Experiment.	
				I.	II.
C ₁₁		132	44·14	43·85	—
H ₁₁		11	3·68	3·89	—
Ag		108	36·12	36·43	35·87
O ₃		48	16·06	—	—
		299	100·00		

Ammonium Salt.—Butyric coumaric acid dissolves easily in ammonia, but the resulting solution when evaporated decomposes, leaving nothing but the acid behind.

From these results there cannot be any doubt, I think, that the new coumarins are really true homologues of the natural body.