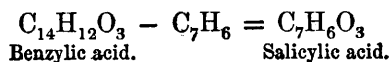
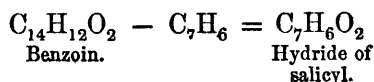


XIV.—*On some new Benzylic Derivatives of the Salicyl Series.*

By W. H. PERKIN, F.R.S.

ON comparing the formulæ of benzoin and benzylic acid with those of the hydride of salicyl and salicylic acid, it will be observed that there exists a difference of C_7H_6 in their composition:—



If, therefore, an equivalent of hydrogen could be replaced by benzyl (C_7H_7) in the salicylic aldehyde and acid, isomers of these substances would be produced.

The following is an account of some experiments which I have made in this direction, and now beg leave to lay before the Society:—

Action of Chloride of Benzyl upon the Hydride of Sodium-salicyl.

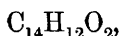
On heating a mixture of equivalent quantities of the hydride of sodium-salicyl (salicylite of sodium) and chloride of benzyl with several times its volume of alcohol, for three or four hours, to a temperature of 120° to 140° C., in a sealed tube, chemical action, takes place, with formation of chloride of sodium.

After filtering off this salt, and separating the excess of alcohol by evaporation, a thick oily substance is obtained, which, when distilled, yields only a small quantity of product below 320° C., by far the larger quantity coming over as a thick yellow oil above the range of the mercurial thermometer. To purify this oily distillate, it is first agitated with a solution of hydrate of potassium, and then with a strong solution of bisulphite of sodium, with which it slowly combines. It should be kept in contact with this reagent for two or three days, with frequent agitation or stirring, otherwise a quantity of product may remain uncombined, and be lost. The crystalline com-

pound thus obtained is collected upon a cloth filter, drained, well squeezed from the excess of bisulphite of sodium, and afterwards dissolved in very cold water. Ether is then added to remove oily impurities, and the clear aqueous solution rendered alkaline with carbonate of sodium. The new body which has been liberated by this reagent is taken up with ether, and, upon evaporating, this ethereal solution is obtained as a colourless viscid oil, remaining fluid for days if left undisturbed, but gradually solidifying if agitated. It may then be rendered perfectly pure by recrystallisation from alcohol. The following combustions of this substance were made:—

- I. ·1832 of substance gave
 ·5331 of CO₂, and
 ·0976 of H₂O.
- II. ·2661 of substance gave
 ·7706 of CO₂, and
 ·1425 of H₂O.
- III. ·2437 of substance gave
 ·7062 of CO₂, and
 ·1253 of H₂O.

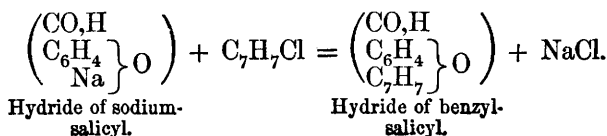
These numbers give percentages agreeing with the formula—



as the following comparisons will show:—

		Theory.		Experiment.		
				I.	II.	III.
C ₁₄	168	79·24	79·31	78·97	79·03
H ₁₂	12	5·66	5·91	5·95	5·71
O ₂	32	15·10	—	—	—
		212	100·00			

This substance represents the hydride of salicyl with its phenolic hydrogen replaced by benzyl. I, therefore, propose to call it the *hydride of benzyl-salicyl*. Its formation may be expressed thus:—



As anticipated, the hydride of benzyl-salicyl is not identical with benzoin, but only isomeric. It melts at 46°C ., benzoin melting at 120°C . With concentrated sulphuric acid it forms a yellow solution, benzoin, under the same circumstances, producing a crimson one. With alcoholic hydrate of potassium it yields a yellow liquid, benzoin giving a violet-coloured reaction.

The hydride of benzyl-salicyl boils at a temperature above the range of the mercurial thermometer. When cold, it possesses a slightly aromatic odour, somewhat similar to that of cloves; but when heated, its vapour is both irritating and suffocating. It is easily soluble in ether, tetrachloride of carbon, benzol, and likewise in boiling alcohol, from which it crystallises on cooling in splendid transparent, flat, oblique prisms. In boiling water it dissolves to a small extent, the solution becoming turbid on cooling, and, after standing, depositing a small quantity of the aldehyde in crystals.

Bromine and also nitric acid attack the hydride of benzyl-salicyl, but the derivatives appear to be uncrystallisable bodies.

As already seen, this body is an aldehyde, and combines with bisulphites. These combinations, however, do not form very easily when pure hydride of benzyl-salicyl is employed, apparently on account of its solid condition, and the insolubility of the resulting compounds in solution of the bisulphites; therefore, it is better to employ the crude oily aldehyde in their preparation. The compound with bisulphite of sodium, when crystallised over sulphuric acid, forms beautiful small micaceous crystals, possessing a very burning taste.

When heated in a sealed tube with acetic anhydride to a temperature of 150°C . for three or four hours, the hydride of benzyl yields an oily product, apparently a direct combination. This compound, if heated with water to 150°C ., decomposes with formation of acetic acid.

Action of Chloride of Benzyl upon Gaultherate of Sodium.

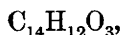
Chloride of benzyl acts easily upon the gaultherate of sodium when heated with alcohol in a sealed tube of 100°C .; four or five hours' digestion being generally sufficient to complete the

reaction. The product on being filtered off from the chloride of sodium which has formed, and evaporated on the water-bath to remove alcohol, yields a rather viscid oil, which, when rectified, gives a considerable quantity of distillate, boiling above 320° C.; this consists of crude benzyl-salicylate of methyl.

To obtain the acid from this product, it is decomposed by boiling with alcoholic hydrate of potassium. On separating the alcohol by evaporation, a crude pasty potassium salt is obtained, floating upon the excess of hydrate of potassium, which remains as a clear fluid, and may be poured away. The potassium salt is then dissolved in water and agitated with ether to remove oily impurities, and the clear aqueous solution decomposed with hydrochloric acid; this causes the new acid to separate as an oil, which solidifies in the course of twenty-four hours. It is then crystallised from alcohol once or twice, or preferably from tetrachloride of carbon. Two combustions of this acid gave the following numbers:—

- I. .2570 of substance gave
 .6929 of CO_2 and
 .1234 of H_2O .
 II. .2452 of substance gave
 .6627 of CO_2 and
 .1224 of H_2O .

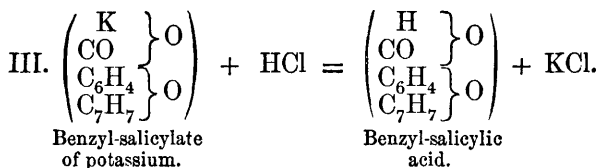
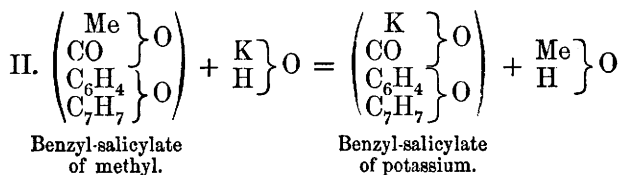
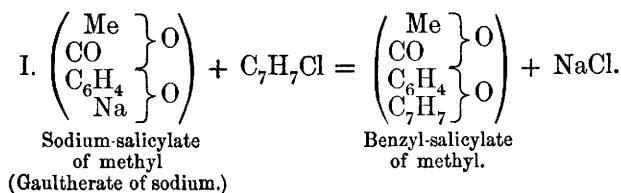
These numbers give per centages agreeing with those required by the formula



as the following comparisons will show:

	Theory.		Experiment.	
			I.	II.
C_{14}	168	73·68	73·53	73·70
H_{12}	12	5·27	5·33	5·54
O_3	48	21·05	—	—
	228	100·00		

This substance represents salicylic acid, in which the phenolic hydrogen is replaced by benzyl. I therefore propose to call it *benzyl-salicylic acid*. Its formation may be expressed thus:—



Benzyl-salicylic acid melts at 75° C., and on cooling forms a viscid oil, which crystallises in a confused manner when rubbed with a glass rod. It is extremely soluble in boiling, and easily so in cold alcohol; it crystallises from this solvent in minute plates. In one experiment a portion of crude acid, dissolved in slightly diluted alcohol, at first deposited an oil, but after standing for about twenty-four hours, beautiful transparent plates of the pure acid, an eighth of an inch in diameter, filled the oily deposit and jutted out into the clear solution. If boiled with water, this acid dissolves to a small extent, and the solution on cooling becomes milky, and, after standing some time, deposits the acid in thin brilliant plates.

Benzyl-salicylic acid is isomeric with benzylic acid, but does not give its coloured reactions, neither does it give the violet coloration of salicylic acid with persalts of iron.

Benzyl-salicylate of Ammonium.—Benzyl-salicylic acid dissolves freely in ammonia, and on boiling off the excess of alkali, a clear solution is obtained, but this, if evaporated to dryness, decomposes with separation of the acid.

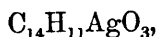
Benzyl-salicylate of Silver.—This body is obtained by the addition of nitrate of silver to the ammonium salt. It is

thrown down as a pure white precipitate slightly soluble in water.

As a small quantity of benzyl-salicylic acid is often carried down with this compound, especially if the ammonium salt employed in its preparation has been boiled rather too much, it should be washed with alcohol as well as with water. It must be dried in vacuo, as it fuses if heated in the water oven. A combustion and silver determinations gave the following results:—

- I. ·1979 of substance gave
·3643 of CO₂ and
·0635 of H₂O.
- II. ·2194 of substance gave
·0694 of silver.
- III. ·1597 of substance gave
·0508 of silver.

These numbers give per centages agreeing with the formula,



as the following comparisons will show:—

	Theory.		Experiment.		
			I.	II.	III.
C ₁₄	168	50·15	50·20	—	—
H ₁₁	11	3·28	3·56	—	—
Ag	108	32·23	—	31·63	31·80
O ₃	48	14·34	—	—	—
	<u>335</u>	<u>100·00</u>			

Benzyl-salicylate of Lead.—The addition of acetate of lead, to a solution of benzyl-salicylate of ammonium, causes the salt to form as a white curdy precipitate.

Benzyl-salicylate of Mercury is a white precipitate.

Benzyl-salicylate of Copper is a pale apple-green precipitate.