VIII.—*New Volatile Organic Acids of the Mountain Ash Berry.*

BY A. W. HOFMANN.

WHOEVER has been engaged in the preparation of malic acid from the juice of the unripe berry of the mountain ash, cannot have failed to perceive the peculiar pungent odour evolved during the evaporation of the liquid partially saturated with lime. Nobody, however, seems to have paid any attention to the body to which this odour belongs, until my friend and former pupil, Dr. George Merck, of Darmstadt, when preparing malic acid on a large scale, had the happy idea of performing the evaporation of the liquid in a distilling apparatus. He obtained in this manner an acid aqueous distillate, from which an oily body of distinctly acid properties could be extracted. Under the name of *Vogelbeer-oel* (mountain ash berry oil), a specimen of this remarkable oil was transmitted to me by Dr. Merck; and since the properties of this substance appeared of such interest as to invite a more minute examination, my friend, anxious to assist in the further elucidation of this matter, undertook the preparation of a larger quantity of the oil. To his kindness I owe the whole of the material employed in the experiments which I am going to describe.

I have received from Dr. Merck the following account of the process by which he has produced the new oil:—

The juice of the unripe berries had been boiled with a quantity of milk of lime insufficient for the saturation of the acid which it contained, and the solution on cooling had deposited the bimalate of calcium. The liquid separated from the crystals was introduced into a copper still, and distilled over an open fire. The condensed vapours furnished a powerfully acid distillate, and when, after some time, the acid reaction of the liquid which distilled over ceased, it could be renewed by pouring a quantity of dilute sulphuric acid into the still. In order to concentrate the acid, the aqueous distillate was saturated with carbonate of sodium and evaporated on the water bath. The residuary semi-solid mass was decomposed in a tall glass cylinder by moderately concentrated sulphuric acid, when the oil rose as a brown layer on the surface of the colourless saline solution. It was dissolved in ether, separated from the

aqueous liquid, and rectified after the ether had been allowed to evaporate.

Several specimens of the mountain ash-berry oil which Dr. Merck had prepared at different periods, exhibited some discrepancies in their properties. Several were of mobile fluidity and scarcely coloured; others brown, nearly black, and considerably resinified. On rectification, however, the oil was obtained colourless. Ebullition commenced at a temperature but little higher than 100°C ; the distillate at this stage of the operation separated into two layers,—oil, which still contained water, floating upon an aqueous solution of the acid. On continuing the distillation, the temperature rose rapidly to 200°C , then more slowly until it reached 225°C . There remained in the retort more or less of a yellowish brown transparent resinous matter. A few distillations soon convinced me that by far the greater bulk of the oil consists of a homogeneous substance, which is, however, very apt to change under various influences.

Freshly distilled, the mountain ash-berry oil constitutes a transparent colourless liquid of a peculiar aromatic odour, not unpleasant when dilute, but rather disagreeable and almost overpowering, when concentrated. The oil has a sp. gr. 1.0681, and boils constantly at 221°C under a pressure of 0.755 m. It is appreciably soluble in water, soluble in all proportions in alcohol and ether. The solutions are strongly acid.

The mountain ash-berry oil has the characters of an acid. It dissolves with facility in the fixed caustic alkalies and in ammonia, also in baryta-and lime-water. Even in carbonate of sodium the oil dissolves, without, however, expelling the carbonic acid. The solutions thus obtained, yield on evaporation dry resinous residues, which indicate no signs of crystallisation. Addition of hydrochloric acid to these residues separates the original oil unchanged. The ammonia-solution furnishes with nitrate of silver a white gelatinous precipitate, which slightly changes colour when exposed to the light.

Two combustions of the oil gave the following results :—

I. 0.2280 grm. oil gave 0.5352 grm. carbonic acid
and 0.1449 grm. water.

II. 0.1926 grm. oil gave 0.4546 grm. carbonic acid
and 0.1280 grm. water.

In the analysis of the silver-compound just mentioned—

0·2465 grm. silver-salt left 0·1209 grm. silver.

The simplest expression for the acid suggested by these data is the formula—

the theoretical values of which I subjoin with the experimental percentages.

	Theory.		Experiment.		Mean
12 equiv. of Carbon	72	64·28	64·01	64·27	64·14
8 „ Hydrogen	8	7·14	7·06	7·38	7·22
4 „ Oxygen	32	28·58	28·93	28·35	28·64
1 equiv. of Oil	112	100·00	100·00	100·00	100·00

In the silver-compound, one equivalent of hydrogen of the acid is replaced by one equivalent of silver. The formula

is supported by the silver-determination above quoted :

	Theory.	Experiment.
Percentage of Silver	49·31	49·05

I should have endeavoured to obtain additional compounds of the oil in order to gain, if possible, further data in favour of the formula which I propose, had not any effort in that direction become superfluous by the observation of the remarkable deportment of the oily acid under the influence of powerful bases and acids.

I have stated that the solution of the oil in potassa furnishes, on addition of a mineral acid, the unchanged oily acid ; the alkaline solution may even be boiled for some time without altering the nature of the substance. But on gently heating the oily acid with *solid* hydrate of potassa, an unexpected transformation takes place. The product of the reaction dissolved in water and saturated with hydrochloric acid, furnishes an oil which rapidly solidifies into a hard crystalline compound, possessing the characters of a well defined acid. This observation at once suggested the idea of aldehyde and acid, but it was found that the transformation takes place without the evolution of a trace of hydrogen. Several grammes of the oil were heated for two or three hours in a sealed tube with

hydrate of potassa in a water-bath. Not a trace of gas was disengaged when, after cooling, the tube was opened under water, but the oil was almost entirely converted into the crystalline acid. The same molecular transformation, as might have been expected, is produced by the action of acids. On boiling the oil for a short time with concentrated hydrochloric acid, it becomes more and more viscid and ultimately solidifies. A similar result is produced by sulphuric acid. The oily acid dissolves in concentrated sulphuric acid: the oil which, is reprecipitated by addition of water gradually becomes a solid crystalline mass.

The mode of forming the new acid suggested the probability of its being isomeric with the original oil. This suggestion has been fully borne out by experiment. I propose to designate this beautiful body by the name of *sorbic acid*, reviving thus a name once used for malic acid. The oily acid may then conveniently be called *parasorbic acid*; for although more directly related to the mountain ash, its character is less defined and salient than that of its derivative.

Sorbic acid is readily purified; being nearly insoluble in cold, and moderately soluble in boiling water, this substance is chemically pure after two or three crystallisations from boiling water. It dissolves with great facility in alcohol or ether. The most appropriate solvent is a mixture of 1 vol. of alcohol and 2 vol. of water. From this liquid the acid separates on cooling in magnificent white needles, often several inches in length. Sorbic acid is inodorous. When in contact with a quantity of water insufficient for its solution, the acid fuses at the temperature of boiling water. The fusing point of dry sorbic acid is $134\cdot5^{\circ}\text{C}$; at a higher temperature the acid distils without decomposition. Sorbic acid is a powerful acid, expelling carbonic acid from all the carbonates.

The composition of sorbic acid was fixed by the following experiments:—

For experiment I. the acid had been dried over sulphuric acid, for experiments II. and III. in the water-bath.

- I. 0·3331 grm. sorbic acid gave 0·7877 grm. carbonic acid
and 0·2160 grm. water.
- II. 0·4065 grm. sorbic acid gave 0·9561 grm. carbonic acid
and 0·2705 grm. water.
- III. 0·3593 grm. sorbic acid gave 0·8500 grm. carbonic acid
and 0·2264 grm. water.

These results lead to the formula

previously established for parasorbic acid.

	Theory.		Experiment		III.	Mean.
			I.	II.		
12 eq. of Carbon	72	64.28	64.49	64.14	64.51	64.38
8 „ Hydrogen	8	7.14	7.20	7.39	7.00	7.20
4 „ Oxygen	32	28.58	28.31	28.47	28.49	28.42
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1 eq. of Sorbic Acid	112	100.00	100.00	100.00	100.00	100.00

The composition of sorbic acid receives additional support from the analysis of several of its salts and derivatives.

Sorbate of Silver. White insoluble pulverulent precipitate obtained on adding nitrate of silver to sorbate of ammonium.

- I. 0.6288 grm. silver-salt gave 0.7488 grm. carbonic acid and 0.1807 grm. water.
- II. 0.4635 grm. silver-salt gave 0.3012 grm. chloride of silver.
- III. 0.6546 grm. silver-salt gave 0.4275 grm. chloride of silver.

To the formula

correspond the following values :—

		Theory.		Experiment.		
				I.	II.	III.
12 equiv. of Carbon	72	32.88	32.48	—	—	—
7 „ Hydrogen	7	3.19	3.19	—	—	—
1 „ Silver	108	49.31	—	48.90	49.15	—
4 „ Oxygen	32	14.62	—	—	—	—
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1 eq. of Silver-salt	219	100.00				

Sorbate of Barium. On boiling carbonate of barium with an aqueous solution of sorbic acid, a neutral solution of the barium-compound is obtained, which yields a crystalline residue on

evaporation. The salt is not much less soluble in cold than in boiling water. It is, however, less soluble in alcohol. The best mode of obtaining it in the pure state consists in adding alcohol to the boiling aqueous solution; on cooling, the sorbate of barium crystallises in scales of silver-white lustre. The salt is anhydrous.

I. 0.4144 grm. of sorbate of barium, dried at 125° C., gave 0.6135 grm. of carbonic acid and 0.1502 grm. of water.

II. 0.2863 grm. of sorbate of barium, treated with sulphuric acid, left 0.1845 grm. sulphate of barium.

The formula

requires

		Theory.		Experiment.	
				I.	II.
12 equiv. of Carbon	72	40.11		40.37	—
7 „ Hydrogen	7	3.90		4.02	—
1 „ Barium	68.5	38.16		—	37.89
4 „ Oxygen	32	17.83		—	—
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1 eq. of Barium-salt	179.5	100.00			

Sorbate of Calcium. Preparation and properties perfectly similar to those of the preceding salt. The formula

was controlled by a calcium-determination.

0.2463 grm. of the salt, dried at 140° C., and treated with sulphuric acid, left 0.1260 grm. sulphate of calcium.

	Theory.	Experiment.
Percentage of Calcium	15.26	15.05

I have not analysed any of the other metallic sorbates; but have made some qualitative observations which may be recorded as contributions to the history of the acid.

The sorbates of *potassium* and of *sodium* are very soluble salts, crystallising with difficulty; the *ammonium*-compound is likewise very soluble, but crystallises beautifully in long slender needles, which are apt to lose part of the ammonia by exposure to the air.

A concentrated solution of the ammonium-compound shows the following deportment with reagents:

Chloride of calcium	.	White crystalline precipitate appearing after a short time.
Chloride of barium	}	No precipitate.
Chloride of strontium		
Chloride of magnesium		
Aluminium-alum	.	White precipitate which dissolves in ether, and is, therefore, nothing but the acid. On ebullition a precipitate is formed which is insoluble in ether, and is probably the sorbate.
Chromium-alum	.	White precipitate of the acid. On ebullition a green amorphous precipitate of sorbate of chromium.
Sulphate of iron	.	Yellowish dingy amorphous precipitate.
Iron-alum	.	Yellow amorphous precipitate.
Sulphate of nickel	.	Greenish amorphous precipitate.
Nitrate of cobalt	.	No precipitate.
Sulphate of manganese	.	Granular crystalline white precipitate, appearing after a few minutes.
Sulphate of zinc	.	White acicular precipitate, which appears after a short time. Insoluble in ether.
Acetate of lead	.	White copious amorphous precipitate.
Nitrate of mercury (Mercurousum)	.	
Chloride of mercury (Mercuricum)	.	
Sulphate of copper	.	Light bluish green amorphous precipitate.

The analytical results obtained in the analyses of the acid itself, and of the silver- barium- and calcium-compounds, are sufficient to

establish the composition of sorbic acid. It remains now but briefly to mention a few experiments made respecting the derivatives of sorbic acid; they are rather fragmentary but may serve to complete the picture of the acid.

Sorbic ether.—Colourless liquid, boiling at $195\cdot5^{\circ}$ C., lighter than water, possessing an aromatic odour similar to that of benzoic ether. It is conveniently obtained by saturating the alcoholic solution of the acid with dry hydrochloric gas. The action of chloride of sorbyl upon alcohol produces the same compound. Sorbate of ethyl contains

as proved by the combustion of the ether.

0·2136 grm. of sorbic ether gave 0·5342 grm. of carbonic acid and 0·1644 grm. of water.

		Theory.	Experiment.
16 equiv. of Carbon	96	68·57	68·21
12 „ Hydrogen	12	8·57	8·55
4 „ Oxygen	32	22·86	—
1 „ Sorbic Ether	140	100·00	

Chloride of Sorbyl is obtained by the usual processes; by the action of pentachloride of phosphorus upon the acid, or of the trichloride upon the potassium-compound. The limited amount of acid at my disposal did not permit me to procure this substance in a state of purity and to establish analytically the formula

assigned to it by theory. But this formula is indirectly proved by the deportment of the crude product, still containing chloride of phosphorus, with water,—when *sorbic acid* is at once reproduced,—with alcohol,—when *sorbic ether* is obtained,—with ammonia and phenylamine,—when respectively *sorbamide* and *phenyl-sorbamide* are generated. The chloride is not volatile without considerable decomposition.

Sorbamide.—This substance is formed by the action of dry carbonate of ammonium upon the crude chloride. It is also produced by digesting sorbic ether with aqueous ammonia in a sealed tube at a temperature of 120°C . At too high a temperature, however, or by protracted digestion, the amide absorbs the elements of water, and regenerates sorbate of ammonium. Sor-

hamide forms white readily fusible needles, soluble in water and in alcohol.

I had scarcely a sufficient quantity for analysis at my disposal, but the following numbers, although exhibiting a slight deficiency in hydrogen, establish the composition of sorbamide :

0.0942 grm. of sorbamide gave 0.2230 grm. of carbonic acid,
and 0.0665 grm. of water.

The formula :

requires

		Theory.	Experiment.
12 equiv. of Carbon	. 72	64.86	64.55
9 „ Hydrogen	. 9	8.10	7.84
1 „ Nitrogen	. 14	12.61	—
2 „ Oxygen	. 16	14.43	—
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1 „ Sorbamide	111	100.00	

Phenyl-sorbamide (Sorbamilide) is obtained by replacing the ammonia in the previous process by phenylamine. After treatment with water, an oily liquid remains which gradually solidifies into a crystalline mass. I have not analysed it, its composition being sufficiently characterised by theory.

When distilled with an excess of hydrate of baryta, sorbic acid exhibits the deportment of the acids with 4 equivalents of oxygen; carbonate of barium being produced, whilst an aromatic hydrocarbon distils over. The limited amount of material has precluded for the present the possibility of a more minute examination of this body.

Sorbic acid is obviously the first term of a new series of well characterised organic acids, closely allied with the ordinary fatty and aromatic acids, occupying, in fact, a sort of intermediate position between the two. On comparing sorbic acid with the terms of the fatty and aromatic acid series containing an equal number of carbon-equivalents, the hydrogen of sorbic acid stands in the middle :

The same remark applies to the carbon, if sorbic acid be contrasted with the fatty and aromatic acids containing an equal number of hydrogen-equivalents :