

UNITED STATES PATENT OFFICE

2,594,379

FLAVORING MATERIALS AND METHOD OF PREPARING THE SAME

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No Drawing. Application September 16, 1950, Serial No. 185,341

18 Claims. (Cl. 99—140)

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This invention relates to flavoring materials and a process for preparing the same. More particularly, it relates to the compounds obtained by reacting aldehydes or ketones with hydrogen sulfide in certain solvents.

Thio-aldehydes and thio-ketones are only imperfectly known in the monomeric state because of the extreme ease with which they go over to odorless polymers. Except for compounds of high molecular weight where steric effects delay polymerization, there are few clear-cut instances in the literature of the isolation of monomers.

When hydrogen sulfide is bubbled through a water solution of an aldehyde or a ketone, a heavy white precipitate of the tri-thio polymer is obtained accompanied by soluble by-products of disagreeable odor. With propylene glycol or glycerin as solvents completely odorless tri-thio polymers are the sole products. Similar results are obtained in benzene, alcohol and ether.

According to the invention it has been found that when this reaction is carried out in an aliphatic ester of a hydroxy polybasic acid as a solvent, the product obtained is a stable solution of a double compound of the carbonyl compound and one molecular proportion of the monomeric thioanalogue. Suitable solvents are, for instance, triethyl citrate, diethyl tartrate, diethyl saccharate and diethyl mucate. Triethyl citrate has several advantages which make it most valuable. It is odorless, tasteless and non-toxic; it is soluble in both water and fats; it does not take up atmospheric moisture; it does not dissolve sugars and has great spreading power on highly soluble foodstuffs, such as dry soluble coffee, without gumming or caking.

To carry out the reaction, hydrogen sulfide is simply bubbled through a solution of the carbonyl compound until the odor of the original compound is no longer apparent. The concentration of the carbonyl compound is preferably 5% or less. The time required varies but it is generally from about 2 to 8 hours. There is no heat evolution and the solutions obtained are completely colorless. The excess hydrogen sulfide is blown out with a stream of nitrogen or other inert gas.

Any aliphatic aldehyde or aliphatic methyl ketone may be used, provided the longest chain does not contain more than 6 carbon atoms. N-hexaldehyde reacts completely whereas n-heptaldehyde will not react at all. Branched chain aliphatic aldehydes containing more than 6 carbon atoms will react providing the longest chain is not more than 6 carbons. Reaction is also

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generally not affected by unsaturation or substitution. Alpha substituted aldehydes give products of comparatively low odor intensity. Reaction velocity is generally proportional to chain length. Cyclohexanone reacts completely while no reaction whatever is shown by cyclopentanone. Aromatic carbonyl compounds do not react whether the carbonyl group is attached to the ring or is in a side chain.

The solutions obtained give no test for the carbonyl group and are ready to use as such for flavor purposes. The odors are in many cases of very high intensity and are much pleasanter than the odor of the average organic sulfur compound. In many cases, also, they are identical with or closely resemble odors of natural products. In practically all cases the solutions are indefinitely stable.

The following table gives the odor character of 5% triethyl citrate solutions of representative carbonyl compounds treated by the process described:

25 Carbonyl Compound	Odor		
	Intensity	Main	Secondary
Formaldehyde.....	moderate..	cauliflower..	onion.
Acetaldehyde.....	strong.....	sauerkraut..	spicy.
Propionaldehyde.....	do.....	onion.....	none.
30 N-Butyraldehyde.....	do.....	grass green..	onion.
Iso-Butyraldehyde.....	feeble.....	onion.....	sweet.
Iso-Valeraldehyde.....	strong.....	bacon.....	green.
N-Hexaldehyde.....	do.....	weedy green..	none.
Alpha-Ethylbutyraldehyde.....	feeble.....	earthy.....	pungent.
2-Ethylhexaldehyde.....	strong.....	mint.....	geraniums.
Acrolein.....	do.....	beef fat.....	green.
35 Crotonaldehyde.....	moderate..	bacon.....	cheese.
Tiglic Aldehyde.....	feeble.....	winey sharp..	meaty.
2-Ethyl-3 Propyl Acrolein.....	strong.....	rank green..	tea-like.
Aldol.....	feeble.....	meaty.....	none.
5-Hydroxypentenal.....	do.....	cucumber... sharp.	sharp.
Beta-Ethoxypropionaldehyde.....	moderate..	burnt cheese.	onion.
Glyoxal.....	strong.....	garlic.....	meaty.
40 Pyruvic Aldehyde.....	do.....	sour.....	burnt.
Cyclohexanone.....	do.....	fresh sour..	onion.
Acetone.....	do.....	sour.....	spicy.
45 Diacetone Alcohol.....	moderate..	do.....	Do.

The products from formaldehyde, acetaldehyde and pyruvic aldehyde have also been obtained by careful fractionation of the low boiling components of freshly roasted coffee.

The products from isovaleraldehyde and crotonaldehyde have been obtained in the methanol eluate of the chromatograph of coffee extract on aluminum oxide.

The product from propionaldehyde is believed to be identical with the compound of very short life obtained by quickly distilling freshly crushed onions (Edward F. Kohmann, Science, 106, 625-7,

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1947). Kohmann tentatively identified has compound as monomeric thio-propionaldehyde. This product is probably the most important of those obtained. The odor is very powerful and is finest pure onion. It has shown no change after storage for many months in triethyl citrate solution.

The product from acrolein is probably closely related to the product responsible for the flavor of cooked meat, if it is not actually one of the substances responsible. Its odor when suitably diluted is hardly distinguishable from the odor of roast beef fat. It is possible its formation in the cooking of meat takes place in the melted fat, the acrolein and hydrogen sulfide coming from pyrolysis of glycerol and the proteins, respectively. The products from crotonaldehyde and isovaleraldehyde have strong, appetizing, cooked bacon odors. As these aldehydes are components of wood smoke, the formation of these compounds in smoked meat by a similar mechanism seems quite plausible.

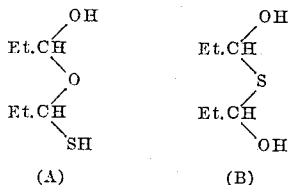
The product from propionaldehyde is representative and responded as follows.

High vacuum distillation from the triethyl citrate solution gave a colorless, odorless oil boiling just under the triethyl citrate. There were no low boiling products. The distillate contained all the sulfur and decomposed into a red, vile smelling oil and a black non-volatile resin on attempted distillation at atmospheric pressure. Chromatography of the triethyl citrate solution on aluminum oxide gave a single narrow band, indicating very probably only a single compound to be present.

Sulfur analysis of the hydrogen sulfide free solution gave very nearly one atom of sulfur absorbed for each two mols. of propionaldehyde originally present. All sulfur was removed quantitatively from solution as lead salt and the air dried weight of the salt indicated 1 mol. of lead to each 4 mols. of propionaldehyde. The lead salt is quantitatively decomposed to PbS in boiling water, which indicates it is not a simple mercaptide. The triethyl citrate solution decolorizes iodine in the cold, using 2 equivalents to one of propionaldehyde (not a simple sulfide).

The product was found to be relatively stable to hot dilute acids but was instantly decomposed by cold dilute alkali to a white amorphous precipitate and propionaldehyde.

These properties indicate 1 mol. of propionthioaldehyde associated with 1 mol. propionaldehyde either in the form of the hemi-acetal (A) or the alpha-alpha dihydroxy sulfide (B).



Structure (B) is more probable because of the similarity in properties to the better known alpha-alpha dichlor-sulfides which owe their instability and peculiar character to the juxtaposition of the two chlorines and sulfur. It is probably the same juxtaposition of hydroxyl and sulfur which give our products their powerful, pleasant odors as compared with the usually disagreeable odors of most organic sulfur compounds.

The products obtained in accordance with the invention may be used for flavoring many food

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products including, for instance, canned and dried soups, vegetable juices, aspice, peanut butter, condiments, pickles, vinegar and cheese. The compounds obtained from propionaldehyde, isovaleraldehyde, acrolein and crotonaldehyde are useful for flavoring meats, and particularly smoked and spiced meats and sausages. The compounds obtained from formaldehyde and isovaleraldehyde are useful as coffee aroma components.

I claim:

1. Process of preparing flavoring materials which comprises passing hydrogen sulfide through a solution of a carbonyl compound of the group consisting of aliphatic aldehydes and aliphatic methyl ketones whose longest chain contains not more than 6 carbon atoms and cyclohexanone, in an aliphatic ester of a hydroxy polybasic acid.

2. Process as claimed in claim 1 wherein the ester is triethyl citrate.

3. Process of preparing flavoring materials which comprises passing hydrogen sulfide through a solution of an aliphatic aldehyde whose longest chain contains not more than 6 carbon atoms in an aliphatic ester of a hydroxy polybasic acid.

4. A stable solution of a double compound of a carbonyl compound of the group consisting of aliphatic aldehydes and aliphatic methyl ketones whose longest chain contains not more than 6 carbon atoms and cyclohexanone with one molecular proportion of the corresponding thio-analog the solvent being an aliphatic ester of a hydroxy polybasic acid.

5. A product as claimed in claim 4 wherein the solvent is triethyl citrate.

6. A stable solution of a double compound of an aliphatic aldehyde whose longest chain contains not more than 6 carbon atoms and one molecular proportion of the corresponding thio-analog the solvent being an aliphatic ester of a hydroxy polybasic acid.

7. Process as claimed in claim 3 wherein the ester is triethyl citrate.

8. A product as claimed in claim 6 wherein the solvent is triethyl citrate.

9. Process of preparing a flavoring material which comprises passing hydrogen sulfide through a solution of propionaldehyde in triethyl citrate.

10. Process of preparing a flavoring material which comprises passing hydrogen sulfide through a solution of isovaleraldehyde in triethyl citrate.

11. Process of preparing a flavoring material which comprises passing hydrogen sulfide through a solution of acrolein in triethyl citrate.

12. Process of preparing a flavoring material which comprises passing hydrogen sulfide through a solution of crotonaldehyde in triethyl citrate.

13. Process of preparing a flavoring material which comprises passing hydrogen sulfide through a solution of formaldehyde in triethyl citrate.

14. A stable solution in triethyl citrate of the double compound composed of propionaldehyde and thio-propionaldehyde.

15. A stable solution in triethyl citrate of the double compound composed of isovaleraldehyde and thio-isovaleraldehyde.

16. A stable solution in triethyl citrate of the double compound composed of acrolein and thio-acrolein.

17. A stable solution in triethyl citrate of the

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double compound composed of crotonaldehyde and thio-crotonaldehyde.

18. A stable solution in triethyl citrate of the double compound composed of formaldehyde and thio-formaldehyde.

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