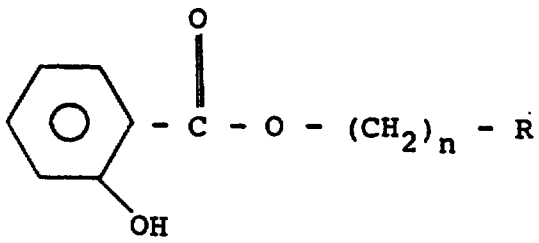
The use of salicylic acid esters as perfumes, perfume compositions containing them and new salicylic esters

This invention relates to perfuming agents, some novel, and to compositions containing them.

Numerous esters of salicylic acid are known from the literature. Some of them, including for example methyl, butyl, amyl, hexyl, benzyl and 3-hexenyl salicylic acid ester, are used in the perfume industry (S. Arctander, Perfume and Flavor Chemicals, 1969; O.Z. Bedoukian, Perfum. Flavor 6 (5) 60-61 (1981)).

A new group of salicylic acid esters distinguished by surprising and valuable perfume properties, particularly by high persistence, has now been found. The group of salicylic acid esters in question are the salicylic acid esters of carbocyclic, non-aromatic alcohols. The esters are characterized by the following general formula



in which

R represents a cycloalkyl or cycloalkenyl group optionally substituted by C_1-C_4-alkyl, the sum of the C-atoms in R amounting to between 5 and 9, and

n = 0 - 3.

By virtue of their pronounced odor profile, the esters in which the sum of the C-atoms in R amounts to between 5 and 6 and n = 0 or 1 are particularly of interest.

The salicylic acid esters are produced in known manner by esterifying salicylic acid with a carbocyclic alcohol as defined in the general formula, optionally in the presence of acidic or alkaline catalysts, the water given off during the reaction being removed, or by reacting salicylic acid chloride with the alkali alcoholate of the carbocyclic alcohol or by transesterifying methyl salicylate with the carbocyclic alcohol.

Some of the compounds corresponding to the general formula are known from the literature although there is no reference there to their properties as perfumes.

Others which have particularly interesting perfume properties are new compounds and, accordingly, are claimed as such.

The odor characteristic of the salicylic acid esters in question is generally flowery with a typical salicylate note, flowery, aromatic, balsamy notes crucially determining the odor profile in individual cases.

The claimed esters may be used as such or combined with other perfumes and/or standard perfume ingredients to form new interesting perfume compositions. To this end, the compounds are used in a quantity of from 1 to 50% by weight, based on the composition as a whole. Compositions such as these may be used for perfuming cosmetics, such as toilet waters, creams, lotions, aerosols, toilet soaps, in extract perfumery and also for improving the odor of industrial products, such as cleaners, disinfectants, fabric treatment preparations and the like. By virtue of their unusual power of radiation and persistence, the esters are particularly suitable for perfuming fabric detergents, fabric softeners and cosmetics. The compositions in question or the esters themselves may be added to the various

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products in quantities of from 0.05 to 2% by weight, based on the product as a whole.

The claimed esters are further distinguished by extremely high stability of their odor profile. They do not produce any unpleasant secondary odors, even after prolonged storage of the products perfumed with them. The cyclopentyl and cyclohexyl esters are particularly preferred for use under practical conditions by virtue of their radiant odor and their persistence coupled with their high stability to aggressive media.

EXAMPLES

General procedure for an esterification process

1 mole of salicylic acid methyl ester and 2 moles of the particular alcohol are initially introduced into a reaction vessel. 18 g (0.1 mole) of a 30% sodium methylate solution are slowly added dropwise with stirring at 60 to 65°C. On completion of the addition, the methanol released is distilled off through a Claisen bridge, the sump temperature rising to approximately 170°C.

On completion of the transesterification reaction, the residue is taken up in water and extracted with ether. The ether extract is washed until neutral, dried over sodium sulfate and concentrated.

The crude product gives the desired ester after distillation through a packed column.

1. Cyclopentyl salicylate (new compound) $B.p._{0.5}$ = 114°C; n_D^{20} = 1.5355

Odor: very strong, sweet, flowery note

2. 2,2,4- (2,4,4-) trimethylcyclopentyl salicylate (new compound, isomer mixture) $B.p._{0.3}$ = 108°C; n_D^{20} = 1.5145

Odor: faint balsamy note

3. 3,3,5-trimethylcyclohexyl salicylate
(CAS Registrg. No. (118-56-9)) n_D^{20} = 1.5188
Odor:faint balsamy note

4. Cyclohexyl salicylate B.p.$_{0.04}$ 115°C
(literature: R. De Fazius and n_D^{20} = 1.5335
G. Berti, Ann. Chimica
41 621-641 (1951)).
Odor: aromatic note with a woody undertone

5. 4-isopropylcyclohexyl salicylate M.p. 48°C
(new compound)
Odor: faint balsamy note

6. Cyclohexyl methyl salicylate B.p.$_{0.01}$ 100°C
(new compound) n_D^{20} = 1.5309
Odor: faint balsamy note

7. Cycloheptyl salicylate B.p.$_{0.01}$ 112°C
(new compound) n_D^{20} = 1.5362
Odor: fine, spicy-balsamy note

8. Cyclooctyl salicylate n_D^{20} = 1.5376
(new compound)
Odor: fine balsamy note

9. cyclooct-4-enyl salicylate B.p.$_{0.01}$ 130°C
(new compound) n_D^{20} = 1.5467
Odor: faint, balsamy, slightly fatty note.

10. Flower complex

Jasmacyclat (R)	35 parts by weight
Jasmonan (R)	25 "
Jasmelia (R)	15 "
Aurantesin B (R)	15 "
Eugenol pure	85 "
Indolene	180 "
Benzyl benzoate	120 "
Benzyl acetate	175 "
Cyclohexyl salicylate	350 "
	1,000 parts by weight

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11. Perfuming of soap

Cyclohexyl salicylate was incorporated in a concentration of 1.5% in neat soap. The forearm of a test subject was washed with the soap for 15 seconds and the odor of the lather assessed. The lather was then rinsed off, the forearm dried and the remaining odor assessed over a period of several hours.

The known perfume, benzylsalicylate, was used for comparison. Power of radiation and persistence were assessed on a scale of 1 to 6,

6 = very strong radiation and persistence
5 = strong radiation and persistence
4 = good radiation and persistence
3 = still noticeable radiation and persistence
2 = very faint radiation and persistence
1 = no radiation or persistence

Table 1

	Odor of lather	Odor of skin
Cyclohexyl salicylate	5	5
Benzyl salicylate (comparison perfume)	3	3

12. Perfuming a fabric softener

0.3% of cyclohexyl salicylate was incorporated as perfume in the formulation of a standard, commercially available fabric softener based on cation-active quaternary ammonium compounds, emulsifiers, viscosity regulators, solvents and diluents.

A formulation perfumed with 0.3% of benzyl salicylate was used for comparison.

Three different cloths of cotton (CN), polyester (PE)

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and cotton/polyester blend (M) were rinsed with 100 ml of this fabric softener in a washing machine. After spin-drying, the cloths were assessed for odor both in moist form and after drying (overnight on a washing line) (cf. Example 11). In addition, the cloths were stored under dry conditions (in polyethylene bags) and reassessed after various periods.

Table 2

	Fabric	Moist	Dried overnight	+24 h	+1 week	+2 weeks
Cyclohexyl salicylate	CN	6	5	5	5	4
	PE	6	6	5	5	4
	M	5	5	5	4	3
Benzyl salicylate (comparison perfume)	CN	4	3	2	3	1
	PE	4	3	2	2	1
	M	3	3	2	2	1

13. Perfuming a detergent

0.15% of cyclohexyl salicylate was incorporated as perfume in the formulation of a standard commercially available heavy-duty detergent based on anionic and nonionic surfactants, builders, complexing agents, perborate, redeposition inhibitors, soil suspending agents, brighteners and fillers. A second sample of the same detergent was perfumed with 0.15% of benzyl salicylate for comparison.

Normally soiled washing was washed with the detergents in a drum-type washing machine using the pre-wash and main wash cycles.

On completion of the pre-wash and main wash cycles, a) the wash liquor was assessed for odor after rinsing and spin-drying the damp washing was assessed for

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odor in the same way as described in Example 12.

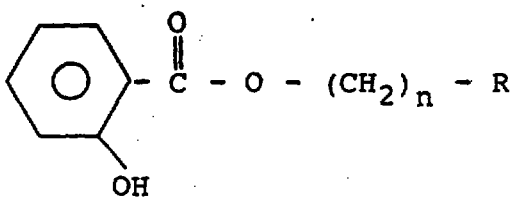
Table 3

	Odor of the wash liquor		
	Pre-wash	Main wash	Damp washing
Cyclohexyl salicylate	5	5	3
Benzylsalicylate (comparison perfume)	2	2	2

* C L M S *

CLAIMS:

1. The use of salicylic acid esters corresponding to the following general formula



in which
R represents cycloalkyl or cycloalkenyl optionally substituted by C_1-C_4-alkyl, the sum of the C-atoms in R amounting to between 5 and 9,
n = 0 - 3,
as perfumes.

2. The use of salicylic acid esters corresponding to the general formula in Claim 1 in which the sum of the C-atoms in R amounts to 5 - 6 and n = 0 or 1.

3. The use of cyclopentyl salicylate or cyclohexyl salicylate as perfumes.

4. Perfume compositions characterized by a content of from 1 to 50% by weight of the salicylic acid esters defined in Claims 1 to 3 together with one or more other perfumes and/or conventional perfume ingredients.

5. Perfume compositions as claimed in Claim 4 substantially as herein described with reference to Example 10.

6. A composition perfumed by the addition of an ester as defined in any of Claims 1 to 3 or a composition as claimed in Claim 4.

7. A composition as claimed in Claim 6 in which the amount of ester or perfume composition added amounts to 0.05 to 2% by weight based on the weight of the composition.

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8. A composition as claimed in Claim 6 or Claim 7 substantially as herein described with reference to Examples 11, 12 or 13.

9. Cyclopentyl salicylate.

10. 2,2,4-(2,4,4)-trimethylcyclopentyl salicylate in the form of an isomer mixture.

11. 4-isopropyl cyclohexyl salicylate.

12. Cyclohexylmethyl salicylate.

13. Cycloheptyl salicylate.

14. Cyclooctyl salicylate.

15. Cyclooct-4-enyl salicylate.