Structure/Odor-Relationships of Longifolene Derived Esters

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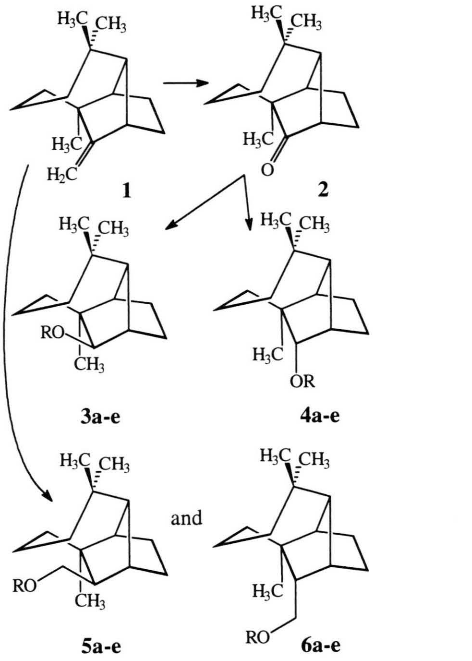
A series of epimeric esters of longicamphenilol and longifolol are prepared and their odorous properties described. It is shown that there are significant differences between the exo- and endo-series. All esters are well accessable starting from longifolene.

Introduction

The sesquiterpene (+)-longifolene (**1**) represents an ideal natural source for the industrial production of modern flavor and fragrance compounds (Ohloff, 1994). It has been found widely distributed and can be produced commercially even in hundred ton quantities, mainly from Indian turpentine oil. Starting from (+)-longifolene (**1**) at least four flavors are commercially available. From (-)-isolongifolene (Dev, 1981), which can be obtained by isomerisation of **1**, about thirteen flavors are industrially produced (Ohloff, 1994). These facts were the cause of the following study on structure/odor relationships. We focused our interest to the olfactory properties of a series of epimeric esters of (-)-exo- and (-)-endo-longicamphenilol (**3** and **4**; R=H), (-)-longifolol (**5**; R=H) and (-)-isolongifolol (**6**; R=H), respectively. All these alcohols are easily obtainable from (+)-longifolene (**1**). Furthermore it should be examined whether there are correlations between stereochemistry and odor.

Results and Discussion

Esters of exo- and endo-longicamphenilol



3: (-)-exo-longicamphenilol **4:** (-)-endo-longicamphenilol
5: (-)-longifolol **6:** (-)-isolongifolol
Esters: (**a**) acetate; (**b**) propionate; (**c**) isovalerate; (**d**) acrylate; (**e**) dimethylacrylate.

The oxidation of (+)-longifolen (**1**) with $KMnO_4$ furnishes (-)-longicamphenilon (**2**) (Weyerstahl and Krohn, 1987) which can be reduced with Na/n-propanol (Dalavoy *et al.*, 1987) or $LiAlH_4$ (Weyerstahl and Krohn, 1987) yielding (-)-endo- or (-)-exo-longicamphenilol (**4** or **3**) respectively. Both epimeric alcohols were converted into the acetate (**3a/4a**), propionate (**3b/4b**), isovalerate (**3c/4c**), acrylate (**3d/4d**) and dimethylacrylate (**3e/4e**) esters. Remarkably the endo-esters (**4a-e**) exhibited a variety of different scents whereas the exo-esters (**3a-e**) were nearly odorless or undefineable (with the exception of **3c**). It seems apparent that the sterical hindrance of the exo-ester group is responsible for the disappointing odorous profile. The pleasant herbal-woody scent of **4a** should be emphasized. Successful development of further longicamphenilol esters therefore seems promising in the endo-series. The odorous properties where summarized in Table I.

Esters of longifolol and isolongifolol

It seems interesting wheather there exists a similar pronounced difference in the odorous proper-

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Table I. Odorous properties of the esters of exo- and endo-longocamphenilol, longifolol and isolongifolol.

Compound	Description[a]
3a	not detectable
4a	herbal-woody
3b	not detectable
4b	unpleasant, "metallic"
3c	unpleasant cheese-like, valerian-like
4c	pleasant cheese-like
3d	not detectable
4d	weak cedar-woody
3e	not detectable
4e	not detectable
5a	cedar-woody, animal
6a	not detectable
5b	flowery, cedar-woody
6b	not detectable
5c	weak flowery-sweet
6c	not detectable
5d	strong mushroom-like, garlic-chive-like bynote
6d	unpleasant mushroom-like, sulphurous
5e	anise-like
6e	anise-like

[a] For description of odors see Müller and Lamparsky (1991) and literature cited therein.

ties of the esters of the C-1 homologue alcohols (-)-longifolol (**5**) (Lhomme and Ourisson, 1968) and (-)-isolongifolol (**6**) (Zeiss and Arakawa, 1954), respectively. Steric hindrance of the ester group in the homologous series should not differ markedly. Surprisingly the esters of the exo-configurated (-)-longifolol (**5a-e**) now exhibited a variety of pleasant aromas, whereas the esters of the endo-configurated (-)-isolongifolol (**6a-e**) possessed generally no remarkable odorous properties (with the exception of **6e**). Further synthesis of esters therefore seem more promising in the exo-series. Finally the well balanced flowery cedar-woody aroma of **5b** should be emphasized. The odorous characters were summarized in Table I.

Experimental Part

The esters were prepared from the alcohols by standard methods either by reaction with the appropriate acid chlorides in the presence of pyridine or by reaction with butyl lithium and subsequent treatment with the appropriate acid chloride (Henecka, 1952). All crude products were submitted to preparative thin layer chromatography and identified by usual spectroscopic methods (IR, MS, ^{1}H-NMR). The odorous characters were determined by the following procedure: The compounds were dissolved in ethanol (10% solution) and paper strips were dipped into the solution. After evaporation of the solvent from the strips the scents of the compounds were evaluated.

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