

New Aroma Compounds from Chirons Isolated from Plant Materials

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Many odoriferous compounds, particularly those isolated from plants, are optically active due to the presence of at least one chiral center in their molecular structure. Optical isomers, or enantiomers, sometimes exhibit different biological and olfactory properties.¹ Therefore, chemists seek to develop simple methods for the preparation of such components and this can be a challenging task. Moreover, data concerning the sensory and biological activity is more meaningful when dealing with a homochiral material than when dealing with a racemic mixture.

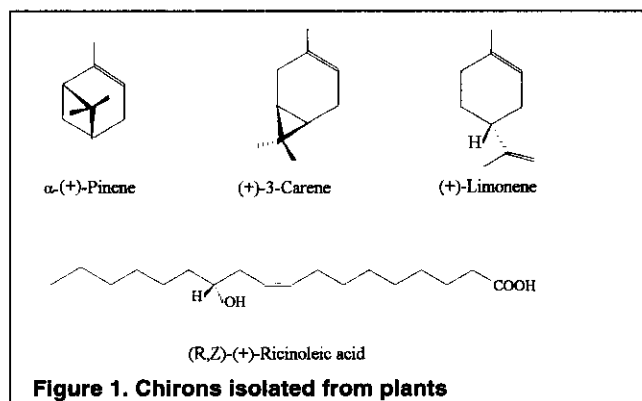
There are several approaches to the preparation of optically active compounds. One of these is to start with chiral starting materials, or chirons, isolated from plants.

This article presents the results of our recent work on the synthesis of novel, optically active odor compounds from chirons isolated from some plant materials. The chirons used were as follows: (+)-limonene, (+)- α -pinene, (+)-3-carene, (+)-longifolene and (+)-ricinoleic acid (Figure 1).

(+)-Limonene is present in citrus peel oils at a concentration of over 90%. It also is a major constituent of the essential oils of caraway, garden dill, horseweed (*Erigeron canadensis*) and goldenrod (*Solidago canadensis*).

(+)- α -Pinene, (+)-3-carene and (+)-longifolene are produced in abundance by the Pinaceae family, and ricinoleic acid is the main ingredient of castor oil from *Ricinus communis*.

In the case of the hydrocarbons we selected as chirons,



the general concept was to convert these to more useful intermediates by the introduction of oxygen functions. For example, the synthesis of the corresponding keto alcohols was effected by ozonolysis and electrochemical reduction of the intermediate ozonides of limonene, α -pinene and 3-carene (Figure 2).²

The method developed is general and allows the preparation of keto alcohols from the substrate materials containing a tri-substituted double bond. These keto alcohols, like the original hydrocarbons, are optically active, although none of them possessed attractive odors.

Lavandulol

Compounds [1], [2] and [3] each have two oxygen-containing functional groups and were converted into mono-oxygenated species in various ways. One of the approaches was the conversion of keto alcohol [1] to (-)-isohomolavandulol using the Wittig reaction as shown in Figure 3.³ This material is a homologue of (-)-lavandulol, which occurs in French lavender oil. Because of the importance of lavandulol, several syntheses of this compound

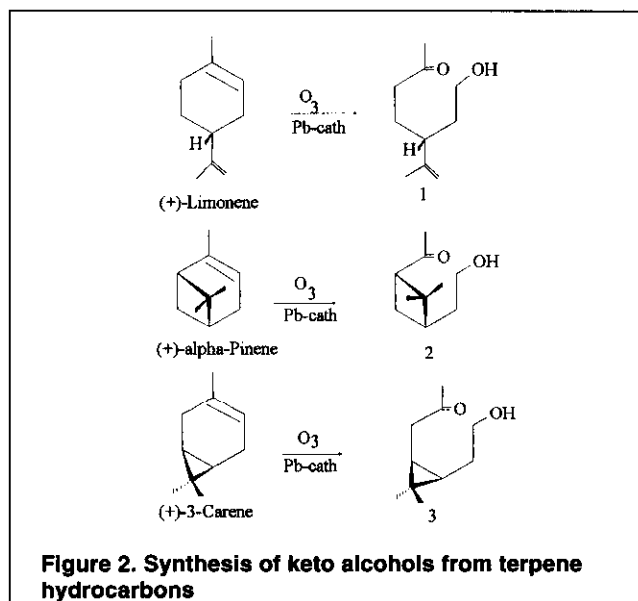


Figure 2. Synthesis of keto alcohols from terpene hydrocarbons

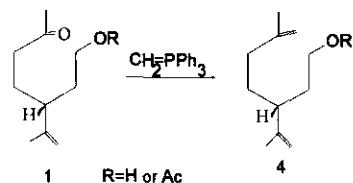


Figure 3. Synthesis of (-)-isohomolavandulol from (+)-limonene

have been reported.⁴ However, these have required a complicated starting material or employed reactions of low regioselectivity. Therefore, investigations directed toward finding new compounds with related odors are justified.

(-)-Isohomolavandulol was found to possess a green, fresh scent similar to that of lavandulol. Its ester can be prepared in the same way from the corresponding ester of keto alcohol [1].⁵ The ester possesses a fresh, herbal and slightly rose odor.

In the course of our work, we observed that treating isohomolavandulol with a dilute sulphuric acid gave a mixture of two cyclic ethers, [5a] and [5b], as shown in Figure 4. This mixture was found to have an intensive lavender scent. The cyclic ethers [5c] and [5d], which are the enantiomers of [5a] and [5b], were obtained from keto alcohols [2] and [3] as shown in Figure 5.⁶

It is worthwhile to note that by starting from enantiomerically pure (+)-limonene or (+)-3-carene, the resultant ethers [5a]/[5b] and [5c]/[5d], respectively, are of high optical purity, as confirmed by chiral gas chromatography.

In light of these results, we decided to separate the mixture of compounds [5c] and [5d] prepared from 3-carene and compare the sensory properties of the pure components with those of their enantiomers [5a] and [5b] synthesized from (+)-limonene. In both cases the isomers were successfully separated on a silica gel column impregnated with silver nitrate.

There was a distinct difference in odors between the compounds derived from (+)-limonene and those derived from (+)-3-carene. Compounds [5a] and [5b]—of R con-

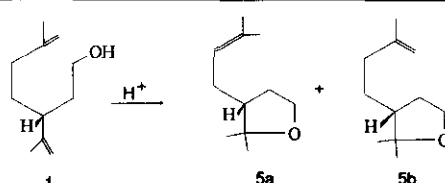


Figure 4. Transformation of isohomolavandulol into tetrahydrofuran derivatives

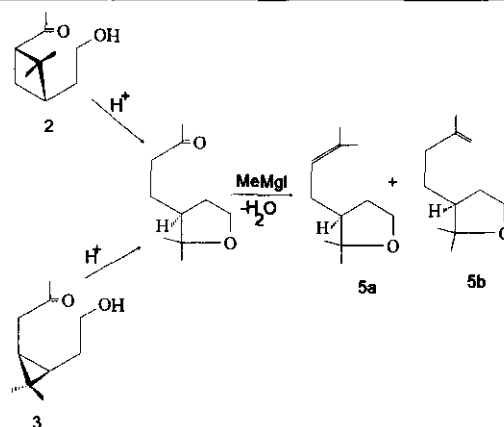


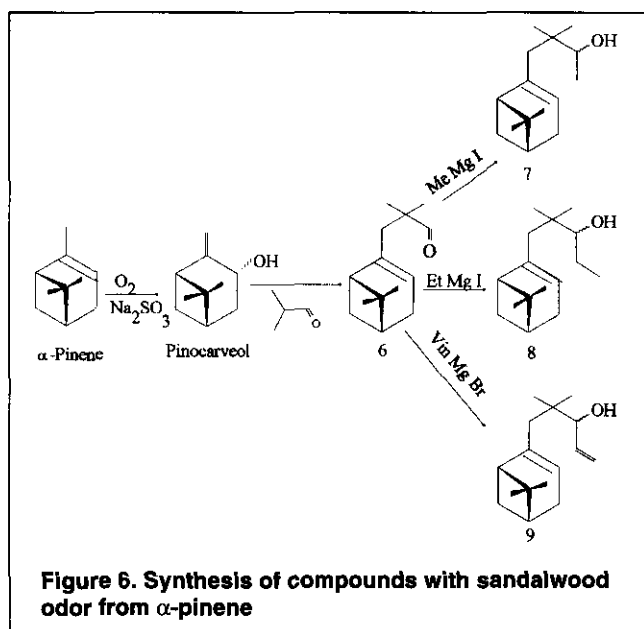
Figure 5. Transformation of keto alcohols into tetrahydrofuran derivatives

figuration and found to be laevorotatory—have a pleasant lavender odor, while their enantiomers [5c] and [5d] clearly demonstrate camphoraceous and cineolic notes. It is possible that these odor differences might result from differences in the impurities produced by the two different synthesis routes. However, we isolated the isomers by chromatographical methods to achieve the highest possible purity. We believe the odor differences were in fact due to enantiomeric differences. This property of optical isomers has been previously reported in the pages of this magazine.⁷

Sandalwood

Many compounds with sandalwood odor have been produced from α -pinene via α -campholenic aldehyde, a compound that has served as a valuable building block for the elaboration of sandalwood aroma materials. Furthermore, it is known from a Swiss patent⁸ and Brunke's reports⁹ that at least two alcohols containing pinane skeleton have a sandalwood smell. Encouraged by this information, we approached the synthesis of new compounds starting from α -pinene, as shown in Figure 6.¹⁰

α -Pinene was photooxidized to deliver pinocarveol. The pinocarveol was then condensed with isobutyraldehyde and, after Claisen rearrangement, aldehyde [6] was produced in a total yield of 90%, based on the α -pinene converted. In the next step, aldehyde [6] was reacted with different Grignard reagents to give a series of secondary alcohols. The structures of some of these ([7], [8] and [9]) can be seen in Figure 6. All the compounds demonstrate a characteristic sandalwood odor.



Amber

From longifolene, we synthesized a new ketone [10] with an amber-like odor.

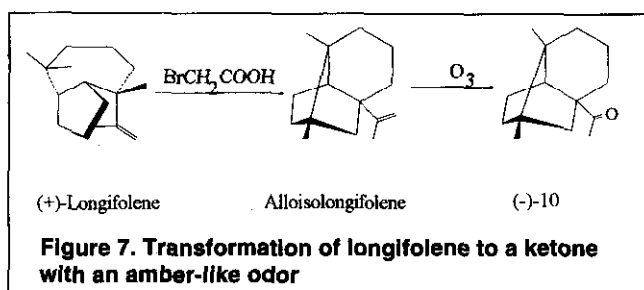
As is well known, the ambergris odor is one of the most appreciated scents in perfumery, which is why many papers

deal with the synthesis of compounds possessing such a smell. The main natural source for producing compounds with an amber-like odor is sclareol. However, its limited availability has stimulated several studies aimed at employing other natural raw materials for synthesis of such compounds. Spanish chemists are the authors of many of these studies.

On the other hand, longifolene is produced by coniferous trees of the Pinaceae family and is one of the most abundant sesquiterpene hydrocarbons. It may therefore represent a good starting material for the synthesis of compounds with an amber-like odor. Ansari, Unwin and Dev, among others, have already produced a number of amber odorants from longifolene and isolongifolene. A new acid-catalyzed rearrangement of longifolene to allosolongifolene was reported in 1983 by Shitole et al.¹¹

In our work, a longifolene-rich fraction¹² (approximately 75% (+)-longifolene), isolated by fractional distillation of the residue of Polish turpentine oil, was transformed into the above-mentioned ketone [10] in a two-step process as shown in Figure 7.¹³

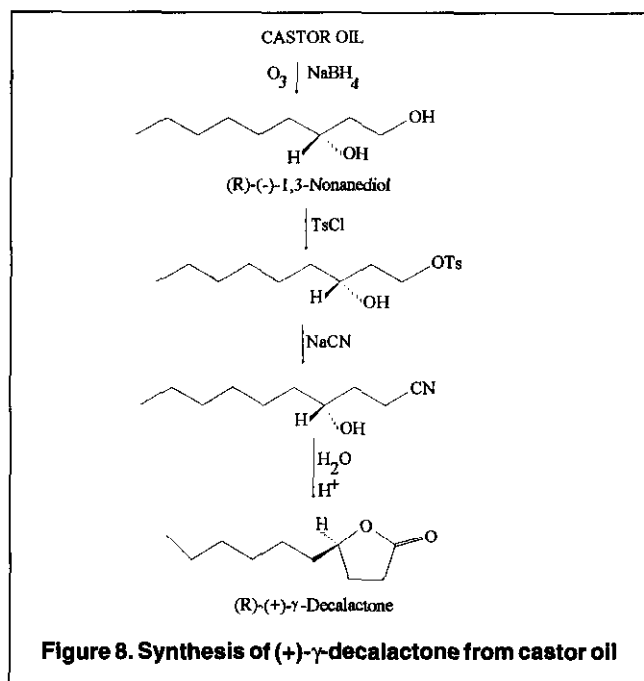
Refluxing longifolene in the presence of a catalytic amount of bromoacetic acid, according to Shitole procedure, resulted in allosolongifolene as the main product. This product was then ozonized to deliver crude ketone [10]. After purification, the ketone appeared optically and olfactorily active. It possesses a distinct amber-like odor



with a little earthy undertone and may be of some interest for perfumers.

γ -Decalactone

Finally, we report our work in synthesizing, from castor oil, an optically active γ -decalactone. It should be emphasized that commercial synthetic γ -decalactone, with a peach aroma, is the racemic form, but that (+)- γ -decalactone—which is a microcomponent of ripe fruits of peaches, nectarines and apricots—has also been made available commercially. It is produced by a microbial process from ricinoleic acid, which is a very costly procedure.¹⁴ Therefore, the search for new, efficient routes to this nature-identical microcomponent may be desirable, and the purpose of one part of our work was to show a simple and cost-effective synthetic way to obtain enantiomerically pure (+)- γ -decalactone.



Castor oil contains up to 90% of optically active (R,Z)-ricinoleic acid or 12-hydroxy-9-octadecenoic acid. The concept for the preparation of (R)- γ -decalactone from castor oil is shown in Figure 8.¹⁵

Oxidation of commercial castor oil provides (R)-1,3-nonanediol in a yield of 72%, based on 85% castor oil. A selective tosylation of the diol with tosyl chloride gives the tosylate in 97% yield. Cyanation of the tosylate and subsequent hydrolysis provides enantiomerically pure R-configured (+)- γ -decalactone in a yield of more than 90%.

This approach, using commercial castor oil as the starting material, has significant advantages and provides a useful alternative to the preparation of (+)- γ -decalactone by microbial and multi-step chemical methods.

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