

Fragrant Esters of 3-Cyclohexyl-1-propanol and 3-Cyclohexyl-1-butanol

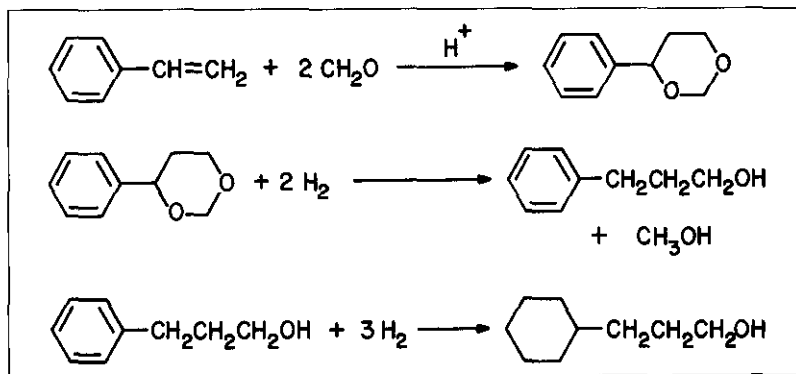
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3-Cyclohexyl-1-propanol and 3-cyclohexyl-1-butanol rank among synthetic fragrant compounds. The fragrant properties of 3-cyclohexyl-1-propanol have been reported in the literature¹ as very mild, sweet balsamic, but rather "flat" odor of moderate to poor ten-

acity. It is less floral than hydrocinnamic alcohol, and does not have the rosy character of that material. The properties of 3-cyclohexyl-1-butanol have been described² in our preceding paper: woody odor of santal type, floral odor.

Both alcohols are obtained by the hydrogenation of the respective phenyl substituted 1-alkanols. The starting raw material for their preparation is styrene or α -methylstyrene, which via the Prins reaction with formaldehyde yields substituted 1,3-dioxans. These, in turn, may be split hydrogenolytically into phenyl substituted 1-alkanols.^{3,4} The preparation of 3-cyclohexyl-1-propanol may be expressed by the accompanying equations.

3-Cyclohexyl-1-butanol was prepared in a similar way from α -methylstyrene.



Preparation and fragrance properties of some esters of 3-cyclohexyl-1-propanol and 3-cyclohexyl-1-butanol are described in this study.

Experimental

Compounds: 3-cyclohexyl-1-propanol was obtained by the hydrogenation of 3-

phenyl-1-propanol,* 3-cyclohexyl-1-butanol was prepared by the hydrogenation of 3-phenyl-1-butanol.* The hydrogenations were performed using nickel on kieselguhr** as the catalyst at 180-190°C, pressure 6.5-10 MPa, or using nickel on alumina*** under the same conditions.⁵

The hydrogenation gave 5-6 wt.% of light foreruns and also 94-95 wt.% of the respective 3-cyclohexyl-1-alkanol. 3-Cyclohexyl-1-propanol (b.p. 108-109°C/1.87 kPa) and

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3-cyclohexyl-1-butanol (b.p. 111°C/1.87 kPa) were redistilled before use.

The acids were commercial[†] and were distilled before use.

Working Procedure: The esterifications were carried out by employing a standard procedure. To 0.6 mol of acid 0.5 mol of the respective alcohol, 1g of p-toluenesulfonic acid and 50 ml of toluene were added. The mixture was heated to boil until water separated from it (usually, four hours); water was removed by means of an azeotropic head. On cooling, the mixture was shaken twice with a 5% solution of sodium carbonate, then with water to neutral reaction. After separation of the organic layer, toluene was distilled off along with the remaining water, and the raw ester was subjected to distillation in vacuo. Purity was checked by gas chromatography. The yields varied around 95% theor. The density of pure esters and the refractive indexes were measured, and the sensoric properties were evaluated.

Results and Discussion

Ten new fragrant esters derived from 3-cyclohexylpropanol and 3-cyclohexyl-1-butanol were prepared.

[†] Lachema Brno

Their physicochemical constants are given in Table I.

Table II summarizes the fragrant properties of the esters. The compounds reported in this study possess interesting fragrant properties and may enrich the assortment of synthetic fragrant compounds used in perfumery industry.

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References

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Table I. Physico-chemical constants of the esters

Compound	b.p. (°C/kPa)	ρ_4^{20}	n_D^{20}
3-cyclohexylpropylformate	106/1.87	0.9440	1.4520
3-cyclohexylpropylacetate	118-119/2.3	0.9309	1.4500
3-cyclohexylpropylpropionate	125.5-126.5/2.2	0.9228	1.4507
3-cyclohexylpropylbutyrate	135.5-136/1.87	0.9145	1.4511
3-cyclohexylpropylisobutyrate	133/1.87	0.9096	1.4487
3-cyclohexylbutylformate	106.5-108.5/1.73	0.9484	1.4582
3-cyclohexylbutylacetate	118.5-120/1.73	0.9351	1.4559
3-cyclohexylbutylpropionate	124-125/1.73	0.9279	1.4565
3-cyclohexylbutylbutyrate	148-149/1.87	0.9189	1.4564
3-cyclohexylbutylisobutyrate	142-143/1.87	0.9153	1.4542

Table II. Fragrance characteristics of the esters

Compound	Fragrance
3-cyclohexylpropylformate	pronounced, green to metallic with cinnamic subnote
3-cyclohexylpropylacetate	ethereal, floral, fruity
3-cyclohexylpropylpropionate	green fruity, resembling fresh bilberries
3-cyclohexylpropylbutyrate	faint, cool green with waxy touch
3-cyclohexylpropylisobutyrate	green, resembling unripe fruit
3-cyclohexylbutylformate	waxy green, resembling iris and galbanum
3-cyclohexylbutylacetate	floral green, herbal
3-cyclohexylbutylpropionate	faintly fruity, somewhat pungent, resembling fermented fruit
3-cyclohexylbutylbutyrate	fruity, faintly green, slightly pungent, remotely resembling galbanum
3-cyclohexylbutylisobutyrate	resembling 3-cyclohexylbutylbutyrate, but more pronounced