

# Syntheses and Odor Characteristic of Beta-Terpinyl Esters

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The terpeneols and their esters are extensively employed in the fragrance and flavor industry. Commercial terpineol is usually prepared by the treatment of terpin hydrate with dilute acid in an aqueous medium. The product comprises largely alpha-terpineol together with about 15% beta-terpineol and 15% gamma-terpineol.<sup>1</sup> It is difficult to separate gamma-terpineol from alpha-isomer and, even using gas-liquid chromatography methods, only partial separation could be achieved.

Commercial terpinyl esters applied in the perfumery and cosmetic industry are usually prepared by esterification of terpineol.<sup>2</sup> The mixture consists alpha-, beta- and gamma-isomers, in which the predominant component is alpha-isomer.

Pure alpha and beta terpineols have different odour properties; therefore, the same phenomenon could be expected for their esters. Physicochemical and odour properties of pure beta-terpinyl esters were not reported in literature. Their synthesis by direct esterification could not be realized because the pure alcohol is not easily available. Our efforts were directed to the synthesis of pure beta-terpinyl esters and comparison of their odour properties with commercial esters containing mainly the alpha isomer.

Our method of synthesis of the beta-terpinyl esters was based on selective elimination of one mole of a carboxylic acid from terpin-1,8 diesters

prepared by acylation of terpin hydrate. The scheme of synthesis is shown in figure 1.

Terpin-1,8(1) obtained from terpin hydrate by azeotropic dehydration in aromatic solvent (benzene, toluene, xylene) was esterified by means of excess of acid anhydride in the presence of the sodium salt of the same acid. The reaction mixture was refluxed until terpin-1,8 disappeared (about 20-30 hours). The progress of the reaction was controlled by the TLC method. After the completion of esterification, the excess of anhydride was hydrolysed by means of a sodium carbonate solution. Then the mixture was neutralized, washed and dried. The solvent was evaporated under reduced pressure, and the residue was fractionated.

We have found that the main products were terpin-1,8 diesters (2) at 65-80%, together with a mixture of isomeric terpinyl esters (3,4,5) at 10-20%, and a small amount of terpenic hydrocarbons. According to the method described we obtained terpin-1,8 diacetate, dipropionate, dibutyrate, divalerate and dibenzoate. We observed that the composition of terpinyl ester fraction is different from commercial product. Using the GLC method we have found that the major component was the beta-isomer (3). The content of beta-terpinyl ester in this fraction was about 70-75% (determined by GLC method).

Reaction conditions, yield of terpin-1,8 diesters and their physicochemical properties are listed in Table I.

Table I. Characteristics of the Reaction Products of Terpin-1,8 with Acid Anhydride

R	Solvent	Reaction time (hr)	Yield of terpinyl ester mixture 3+4+5	Yield of terpin-1,8 diester 2	Physicochemical properties of terpin-1,8 diester			Notes
					B.p./pressure °C/Tr	20 n <sub>D</sub>	M.p.	
CH <sub>3</sub>	-	1	18%	65%	108-10/0.6	1.4530	-	triple excess of acetic anhydride was used
CH <sub>3</sub>	benzene	20	15%	80%	122-5/5	1.4528	-	
C <sub>2</sub> H <sub>5</sub>	toluene	26	12%	70%	99-100/0.4	1.4556	-	
C <sub>3</sub> H <sub>7</sub>	toluene	29	20%	65%	113-16/0.4	1.4587	-	
C <sub>4</sub> H <sub>9</sub>	benzene	30	25%	60%	113-5/0.4	1.4602	-	
C <sub>6</sub> H <sub>5</sub>	xylene	31	50%	30%	-	-	124-5°	crystallized from n-heptane

Table II. Characteristics of the Products of Elimination Obtained from Terpin-1,8 Diesters

R	Reaction Temperature °C	Reaction Time (hr)	Yield of terpinyl ester in relation to diester converted	B.p/pressure °C/Tr	20 n <sub>D</sub>	Content of beta-isomer in the mixture estimated by GLC
CH <sub>3</sub>	137	16	50%	40-2/0.1	1.4652	75%
CH <sub>3</sub>	143	60	60%	75-8/1.8	1.4654	80%
C <sub>2</sub> H <sub>5</sub>	160	20	75%	106-10/17	1.4630	85%
C <sub>3</sub> H <sub>7</sub>	170	11	69%	65-72/0.5	1.4608	89%
C <sub>4</sub> H <sub>9</sub>	170	10	73%	80-4/0.2	1.4628	94%
C <sub>6</sub> H <sub>5</sub>	190	7	75%	115-20/0.2	1.5195	95%

Table III. Comparison of Physicochemical and Odour Characteristics of Pure beta-Terpinyl Esters and Commercial Terpinyl Esters

Pure beta-Terpinyl Esters				Commercial Terpinyl Esters		
B.p/pressure °C/Tr	20 n <sub>D</sub>	Odour	Ester	B.p/pressure °C/Tr	20 n <sub>D</sub>	Odour
71-2/1.8	1.4632	pleasant, sweet odour with hyacinth note, balsamic, intensive, tenacious	Acetate	220/760	1.4657	mildly herbaceous, sweet and refreshing odour of spicy bergamot-lavender type with variations into piney notes
59-61/0.4	1.4610	pleasant floral odour with lavender note, intensive, tenacious	Propionate	240/760	1.4660	sweet-herbaceous, mildly fruity piney, refreshing odour of moderate tenacity
70-1/0.5	1.4608	pleasant, tenacious odour with bergamot-lavender note, moderate intensity	Butyrate	246/760	1.4656	balsamic-floral, sweet and mild, slightly fruity-herbaceous odour of moderate tenacity
108-10/0.4	1.5242	weak but tenacious, pleasant balsamic-floral odour	Benzoate	320/760	1.5290	weak/tenacious, woody-floral, warm odour with a musky undertone

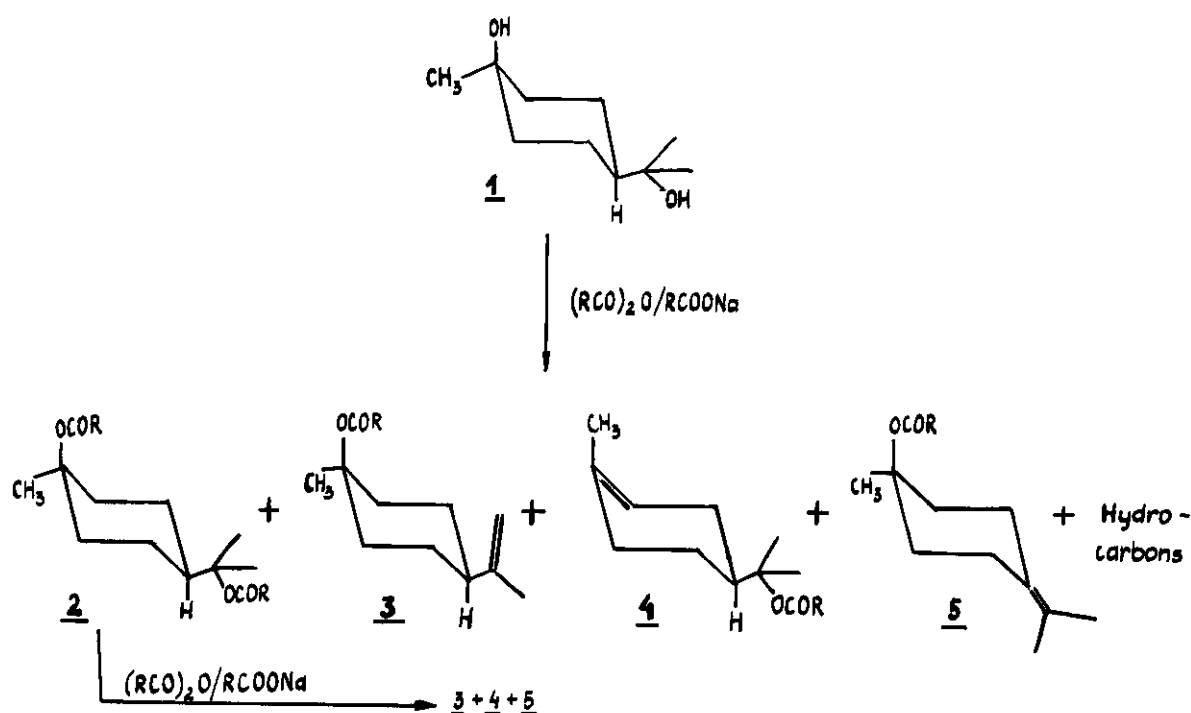


Figure 1. Scheme of terpinyl esters synthesis from terpin hydrate (Where R = CH<sub>3</sub>; C<sub>2</sub>H<sub>5</sub>; n-C<sub>3</sub>H<sub>7</sub>; n-C<sub>4</sub>H<sub>9</sub>; C<sub>6</sub>H<sub>5</sub>)

Pure terpin-1,8 diesters were subjected to the elimination of one mole of acid. The reaction was carried out at elevated temperature (140-180°) in the corresponding acid anhydride medium in the presence of the sodium salt of the same acid. Progress of the reaction was controlled by the TLC method and the process was stopped when terpenic hydrocarbons appeared in the reaction mixture. The excess of anhydride and acid was neutralized by means of sodium carbonate solution. Then the mixture was washed and dried. The product was rectified under reduced pressure using an efficient column. We have found that the main product is the mixture of terpinyl esters (3,4,5) containing beta-isomer (3) as the predominant component. The yield of esters was about 70-75% based on converted terpin-1,8 diesters. We have observed increase of elimination selectivity with the acid chain lengthening. The content of beta-terpinyl esters in the mixtures obtained according to our method has increased from 70% for acetate to 95% for n-valerate.<sup>3</sup>

Elimination conditions, yield of terpinyl esters and their physicochemical properties are listed in Table II.

Pure trans-beta-terpinyl esters have been isolated from the mixture by rectification using a Fischer Spaltrohr column. Their structure was confirmed by IR, MNR and MS analysis. Their physicochemical and odor characteristics in comparison to commercial terpinyl esters are given in Table III.

Our method of synthesis of terpin-1,8 diesters and eliminating one mole of acid made it possible for the first time to produce beta-terpinyl esters with interesting odour properties. This represents a major expansion of the variety of perfumery synthetics produced from turpentine.

#### References

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