BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (1), 261—262 (1979)

Autoxidation of Thujopsene in Carboxylic Acid Media. Co-preparation of Mayurone and 3-Thujopsanone

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(Received May 22, 1978)

Synopsis. *cis*-(−)-Thujopsene has been autoxidized by perculation molecular oxygen through carboxylic acid solution, giving mayurone and 3-thujopsanone in fair yields. An investigation on the reaction conditions is described.

In a previous paper,[1] the autoxidation of thujopsene (**1**) to mayurone and other carbonyl compounds was reported utilizing metal chelate catalysts in dioxane. The reaction of thujopsene however, with a bismuth(III) sulfate catalyst in carboxylic acid media gave a neopentyl type ester (**2**),[2] which differed from the general reactions of olefins.[3] This paper reports the autoxidation of **1** in carboxylic acid media to give mayurone and 3-thujopsanone in fair yields.

Experimental

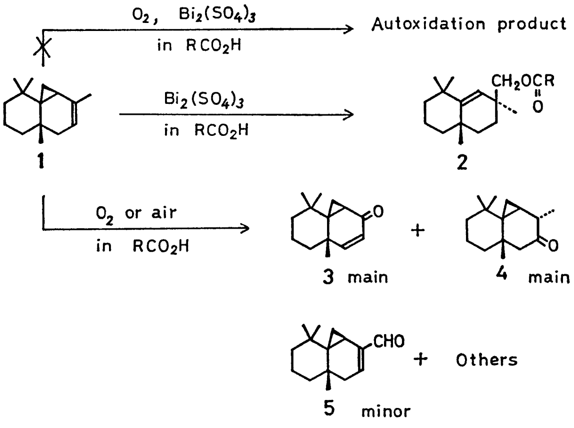
Melting points were determined with a Shimadzu micro melting point apparatus and are uncorrected. The NMR spectra were recored on a JEOL JNM-PMX spectrometer using TMS as the internal standard. The IR spectra were determined on a Shimadzu IR-400 spectrometer and optical rotations on a Shimadzu polarisacchari meter. GLC analyses were performed on a Shimadzu GC-4B apparatus with a 1.5 m glass column packed with 10% OV-17, at 200 °C. The thujopsene used was purified by distillation of Cedar H oil (Takasago Perfumery Co., Ltd.) through a concentric column; bp 120 °C/10 Torr. The organic acids used were commercial, extra-pure reagents.

*General Procedure for Autoxidation of Thujopsene (**1**) in Carboxylic Acid.* Into a stirred solution of **1** (4.09 g, 20 mmol) in an organic acid or dioxane (0.4 mol), was passed a stream of dry oxygen at a rate of 66 ml/min at 75 °C for 20 h, using a catalyst in some cases. After removal of the organic acid under reduced pressure, the solution of the resulting residue was washed with water, the ether layer dried over anhydrous sodium sulfate, and the solvent removed. The reaction mixture was analyzed by GLC. In the case of preparation of main products, the reaction mixture was distilled. The corresponding fractions were collected and subsequently recrystallized.

*Isolation of (−)-3-Thujopsanone (**4**).* Into a stirred solution of thujopsene **1** (30.7 g, 0.15 mol) in propionic acid (333 g, 4.5 mol), a dry stream of oxygen was passed at the rate of 200 ml/min at 75 °C for 30 h. After removal of propionic acid under reduced pressure, the reaction mixture was distilled through a concentric column to collect the distillate with a bp of 138—139 °C/8 Torr on chilling a crystalline matter deposited. Recrystallization of the crystals from pentane gave 2.6 g of **4** as colorless crystals, further purified by sublimation; mp 71.3—71.8 °C; $[\alpha]_D^{20}$ −85.5° (*c* 16.4, CCl_4); IR (CCl_4) 1712 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.61 (3H, s, CH_3), 1.10 (3H, s, CH_3), 1.23 (6H, d, $2CH_3$, J=6 Hz), 1.66 (1H, d, 4-CH_2(α), J=14 Hz), 2.22 (1H, d, 4-CH_2(β), J=14 Hz), 2.45 (1H, q, 2-H, J=7 Hz). Found: C, 81.61; H, 10.88%. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98%.

Results and Discussion

The oxidation of *cis*-(−)-thujopsene (**1**) with molecular oxygen in a series of organic acids from acetic to isovaleric gave mayurone (**3**) and (−)-thujopsanone (**4**) in yields as shown in Fig. 1. The reactions always gave **3**, **4**, and **5**, regardless of the carboxylic acid used. The highest yields were obtained in propionic acid which has the highest pK_a value in the series of organic acid used. Addition of $CoCl_2 \cdot 6H_2O$ in the above reaction system (in $C_2H_5CO_2H$) did not influence the



Scheme 1.

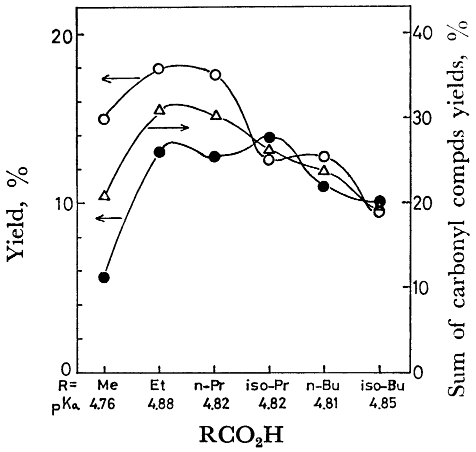


Fig. 1. Yield of carbonyl compounds—carboxylic acid profiles for the autoxidation in carboxylic acid media. Thujopsene 20 mmol, RCO_2H 0.4 mol, O_2 66 ml/min, at 75 °C for 20 h.

○: Mayurone, ●: 3-thujopsanone, △: sum of carbonyl compds.

yields of **3** and **5** but decreased the yield of **4**. Benzoyl peroxide did not give catalytic effect.

The autoxidation without catalyst in dioxane was significantly different from the same reaction in organic acid media. The addition of Co(II) complex catalyst in the system gave a higher yield of **3** and only a little of **4**,[1] the results of which are summarized in Table 1.

TABLE 1. AUTOCATALYTIC OXIDATION OF THUJOPSENE (20 mmol) AT 75 °C FOR 20 h UNDER PERCULATING OXYGEN (66 ml/min)

Reaction		Distribution of products, %	
	Mayurone **3**	(−)-3-Thujopsanone **4**	Thujopsenal **5**
In $C_2H_5CO_2H$	20.2	13.2	0.6
In $C_2H_5CO_2H$,			
$CoCl_2 \cdot 6H_2O$ 2 mmol	16.7	1.1	0.3
4 mmol	20.9	1.1	0.6
6 mmol	22.1	1.2	0.6
10 mmol	20.8	1.0	0.5
In $C_2H_5CO_2H$,			
BPO 0.2 mmol	17.4	12.3	0.4
1 mmol	17.0	11.0	0.6
In dioxane[a]	1.7	2.1	0.6
In dioxane			
Co(II) complex[a]	27.4	5.6	4.9

a) This work, *cf.* Ref. 1.

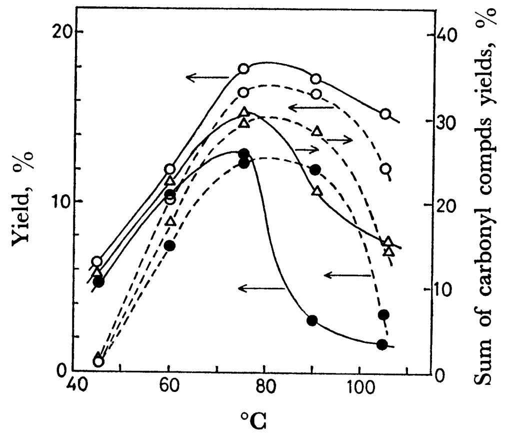


Fig. 2. Yield of carbonyl compounds—reaction temperature profiles for the autoxidation in carboxylic acid media.
Thujopsene 20 mmol, propionic acid 0.4 mol, O_2 or air 66 ml/min for 20 h.
○: Mayurone, ●: 3-thujopsanone, △: sum of carbonyl compds, ——: O_2, ----: air.

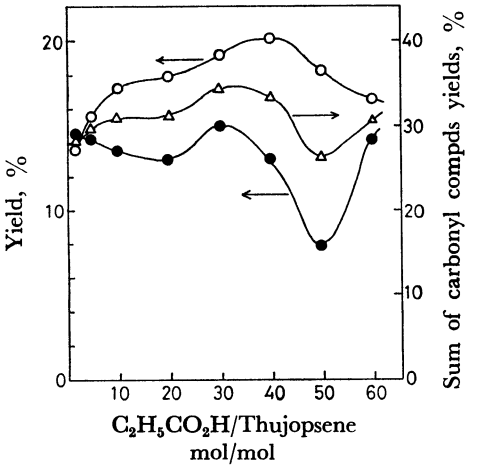


Fig. 3. Yield of carbonyl compounds—amount of carboxylic acid used profiles for the autoxidation in propionic acid media.
O_2 66 ml/min, at 75 °C for 20 h.
○: Mayurone, ●: 3-thujopsanone, △: sum of carbonyl compds.

The optimum conditions for autoxidation were found in propionic acid. To obtain higher yields of carbonyl compounds, the reaction must be conducted at 70 °C using 40—30 mole parts of thujopsene as shown in Figs. 2 and 3.

The GLC of the reaction product (propionic acid/thujopsene=40/1, oxygen 66 ml/min, 75 °C for 20 h) indicated that the main products were **3** and **4**. The IR and NMR spectra of products **3** and **5** were coincident with those of authentic samples. The structure of **4** was confirmed by analytical and spectral analysis and also by the LAH reduction of **4** which afforded (+)-3-neothujopsanol which have been prepared by the hydroboration of thujopsene.[4] It was found that an unidentified product of the autocatalytic oxidation[1] of thujopsene with metal chelate catalyst was identical with (−)-3-thujopsanone (**4**).

The authors wish to express their gratitude to Takasago Perfumery Co., Ltd., for the donation of crude thujopsene.

References

1) M. Ito, T. Nishimura, and K. Abe, *Bull. Chem. Soc. Jpn.*, **45**, 1914 (1972).
2) K. Abe and M. Ito, *Bull. Chem. Soc. Jpn.*, **51**, 319 (1978).
3) S. Suzuki, Y. Moro-oka, and T. Ikawa, *Chem. Lett.*, **1976**, 29.
4) S. P. Acharya and H. C. Brown, *J. Org. Chem.*, **35**, 3874 (1970).