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Note

Conversion of sabinene to phellandral *via* *p*-menthane-1,2,7-triol

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The essential oil of the seeds of *Zanthoxylum rhetsa* DC, which contains 72.7% sabinene, after treatment with peracetic acid has been analysed by GC and GC-MS. Twenty three compounds have been identified with *p*-menthane-1,2,7-triol (36.65%), as the major constituent. The triol on heating with 50% H_3PO_4 forms phellandral (*p*-menthane-1-en-7-al).

Keywords: *Zanthoxylum rhetsa*, Rutaceae, Mullilam, essential oil, chemical transformation, *p*-menthane-1,2,7-triol, phellandral

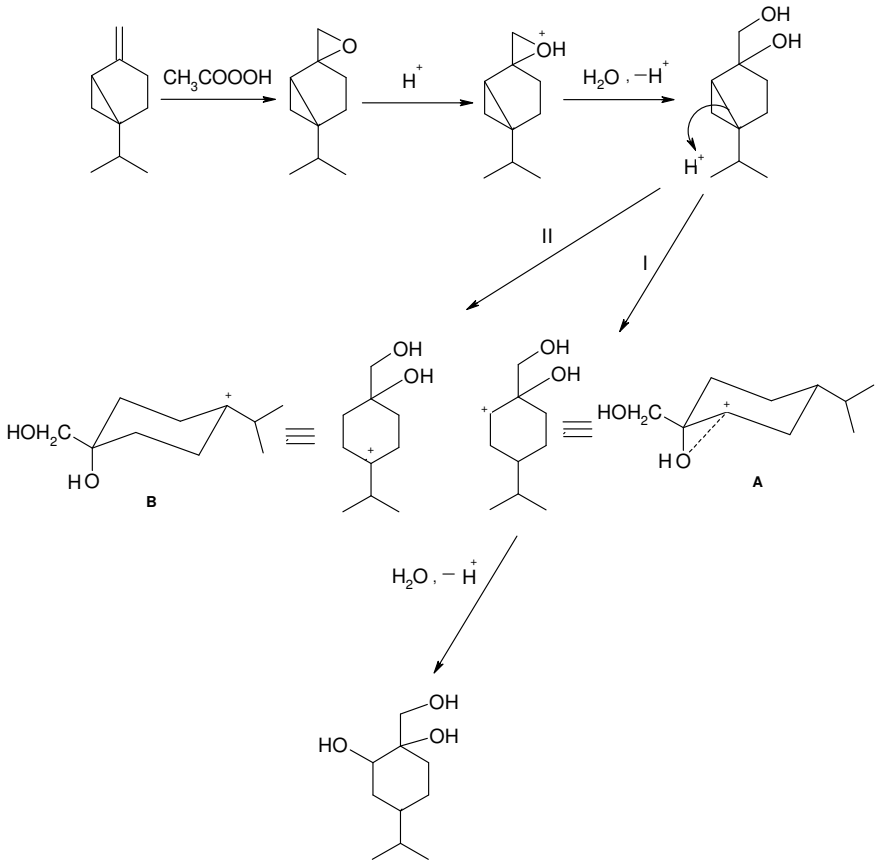
Zanthoxylum rhetsa (Rutaceae family) is a lofty, deciduous tree, up to 35 m. tall, commonly found in the evergreen monsoon forests of the foothills of Assam and Meghalaya and in the eastern and western ghats in peninsular India. The fruits yield an essential oil called Mullilam oil, which is obtained by steam distillation of the dried ripe fruits. The oil has pleasant odour resembling that of sweet orange and tangerine. It is used in the indigenous system of medicine for the treatment of cholera[1]. The oil is also used as an antiseptic, a disinfectant, and for the treatment of asthma, toothache and rhuematism[2]. Earlier works[3-7] revealed that the seed oil was rich in monoterpenes, especially sabinene; while caryophyllene oxide was the major component of the leaf oil. Paknikar and Kamat[8] isolated a crystalline compound from *Z. rhetsa* fruit oil and assigned its structure as 1*S*, 2*S*, 4*S*-trihydroxy-*p*-menthane. It was found to be identical with the compound prepared by Hikino[9] by the action of peracetic acid on sabinene. In the present work, *Z. rhetsa* seed essential oil obtained by steam distillation from alkaline medium, with 72.7% of sabinene content[10] on treatment with peracetic acid became highly viscous. It was then subjected to GC-MS analysis. Comparison of the mass spectral data with those available in the in-house library revealed the presence of *p*-menthane-1,2,3-triol (**Scheme I**) as the major component. This is in contrast with Hikino's observation. The present work was therefore envisaged to investigate further on this.

Experimental Section

The fresh greenish black seeds of *Z. rhetsa* were collected from Malappuram district of Kerala, India. The fresh seeds (310 g) on steam distillation (3 hr) from alkaline solution (500 mL of 10% Na_2CO_3, *p*H ≈ 9.5), without powdering or maceration produced essential oil with a yield of 1.42%.

Essential oil (5 mL, 4.4 g) of *Z. rhetsa* seed was stirred with 36 mL of peracetic acid[11] at RT (30°C) for 24 hr. The solution was poured into cold water, which turned milky. This was extracted with diethyl ether (2 × 100 mL) and neutrallized with 100 mL 10% Na_2CO_3. The ether layer was washed with water and dried using anhydrous sodium sulphate. The solvent on evaporation yielded a highly viscous, pale yellow oil (3.3 g, 76%). It was then column chromatographed (3 cm × 100 cm; d × l) on silica gel (60-120 mesh), using pet.ether, 10:1 mixture of pet.ether-acetone and acetone as eluents. Fractions of 50 mL were collected and homogeneity of each fraction was checked by TLC. Identical fractions were pooled together and concentrated by evaporation. The highly viscous yellow oil (2.9 g) obtained by elution with acetone was used for further study.

Viscous yellow oil (3 mL, 2.9 g) obtained by elution with acetone was refluxed with 10 mL 50% H_3PO_4 for 3 hr. It was cooled, extracted with diethyl ether, washed the ethereal layer with water, dried with anhydrous sodium sulphate and the solvent removed by evaporation. The orange red oil 1.5 g (51.3%), thus obtained, was chromatographed (3 cm×100 cm; d×l) over silica gel (60-120 mesh) and eluted with pet. ether followed by a mixture of pet. ether-ethyl acetate. Fractions 1 to 10 collected using 8:1 pet. ether-ethyl acetate mixture were concentrated by evaporation. Further purification of this compound was carried out by treatment with saturated sodium sulphite solution and shaking well for half an hour. The solid bisulphite product was washed with ether and then decomposed by dil. HCl. It was again extracted with diethyl ether



Scheme I

and washed till acid free, dried and concentrated by evaporation of the solvent. The yellow oil 0.5 g (17%) thus obtained, having pleasant odour, was analysed by GC-MS.

GC analysis was carried out using a Shimadzu GC-14A with FID and the integrator C-R6A-Chromatopac and a Varian GC-3700 with FID and the integrator C-RIB-Chromatopac (Shimadzu Co.). As columns, one 30 m × 0.32 mm bonded non polar FSOT-RSL-200 fused silica (film thickness 0.25 μm, Biorad Co.) and another 30 m × 0.32 mm bonded polar stabil wax (film thickness 0.50 μm; Restek Co.) were used. Carrier gas used was hydrogen. Injector temperature: 250°C, detector temperature: 320°C. Temperature programme was 40°C/ 5 min to 280°C/ 5 min with a heating rate of 6°C/ min. Quantifications were done by Percent Peak Area calculations (non polar column).

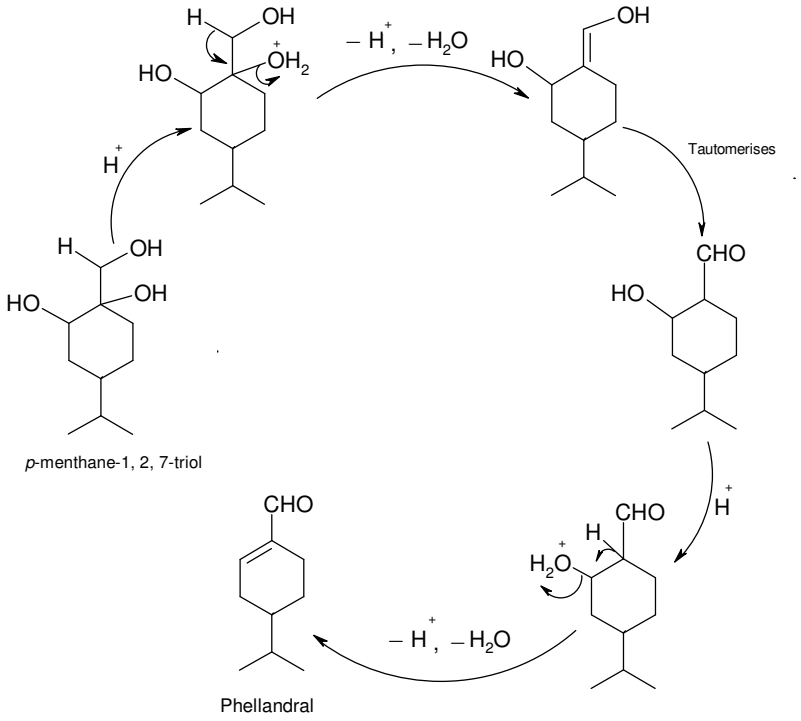
The sample was analysed by GC-MS system also. Shimadzu GC-17A with QP 5000 and the data system Compaq-ProLinea (Class 5k-software) Shimadzu GC-17A with QP 5050 and data system Pentium-II (Böhm Co., Class 5k-software) Hewlett-Packard GC-HP 5890 with HP 5970 MSD and PC-Pentium (Böhm Co., Chem station-software and Finnigan MAP GCQ with data system Gateway-2000-PS75 (Siemens Co., GCQ-software) were used for analysis.

Carrier gas used: helium, injection temperature: 250°C, interface-heating: 300°C, ion-source heating: 200°C, EI mode, scan range: 41-450 amu. For compound identifications Wiley, NBS and NIST library spectra (on-line) as well as reference MS spectral data were used[12-16].

Results and Discussion

The GC and GC-MS analysis of the *Z. rhetsa* seed essential oil, obtained by steam distillation from alkaline medium, on reaction with peracetic acid, showed the presence of 23 compounds, of which *p*-menthane-1,2,7-triol was the major component (36.65%) identified.

Sabinene, the main component present in the *Z. rhetsa* seed essential oil, on reaction with peracetic acid got converted into a triol. This was reacted with



Scheme II

50% H_3PO_4 as explained in the experimental section. The product obtained, on GC-MS analysis contained phellandral (*p*-menthane-1-en-7-al) as major component (82%). The formation of phellandral in this reaction is possible only if *p*-menthane-1,2,7-triol is present in the starting material, while *p*-menthane-1,2,3-triol or *p*-menthane-1,2,4-triol can not yield this product. The formation of *p*-menthane-1,2,7-triol from sabinene, is given in **Scheme I** and its conversion to phellandral in **Scheme II.**

Though a 3°carbocation is more stable than a 2°carbocation, pathway (I) leading to a 2°carbocation is stabilized by the presence of adjacent — OH group as shown, while pathway (II) cannot be stabilized by this way. Carbocation A formed in pathway (I), on reaction with water leads to the formation of *p*-menthane-1,2,7-triol.

This work has generated enough proof that peracetic acid treatment of sabinene gives *p*-menthane-1,2,7-triol that is in contradiction to earlier findings. Phellandral is the major component present in the final product, which finds use in flavour and fragrance industry[17].

Acknowledgements

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