A Comparative Study of the Autoxidation of Δ^3-Carene, α-Pinene, β-Pinene and (+)-Limonene

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A comparison of the rates of autoxidation of the four most commonly occurring terpenes in technical turpentine is a question of technical interest, but as oxidized turpentine is aggressive to sensitive human skin [1], the oxidation rates are of importance for dermatological research. In a preceding series of communications, the present authors have given the experimental conditions for this investigation. These necessitate having a method to investigate the homogeneity [2,3] and a way to purify [4,5] the individual terpenes. However, the inhibiting or accelerating influence of minimum impurities, which cannot be detected by the sorption method has not of course been taken into consideration.

The four terpenes, freshly distilled, were prepared in a state of index homogeneity giving the sorptograms; Δ^3-carene $n_D^{25} =$ 1.4700US, 1–7, α-pinene 1.4632US, 1–7, β-pinene 1.4762US, 1–7 and (+)-limonene 1.4703US, 1–7. Twenty-gram samples were added to four oxidation apparatus assembled side by side on a wooden stand (*cf.* Blohm and Widmark [6]) which were kept at room temperature (22±2°C) and in diffuse daylight *. The consumption of oxygen was measured daily, and at the same time the oxidation vessels were removed and weighed. The samples were analysed by sorption and iodine titration, and the viscosity,

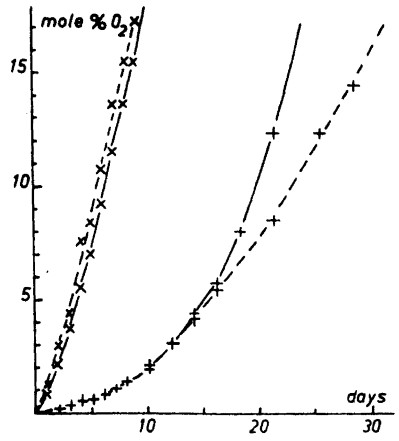

Fig. 1. Rates of oxidation of Δ^3-carene (×) and (+)-limonene (+) and peroxide content from iodine titration (broken lines).

the density and the optical rotation were determined. (In order to save material, these determinations were not made every day.) A small sample was saved for medical investigations. After the determinations, the liquids were replaced in the oxidation vessels which were reweighed, usually indicating a loss of 0.1 g *. The vessels were reconnected to the oxidation apparatus which were totally refilled with oxygen, *cf.* Lombard [7]. Care was taken to prevent contaminations within the four terpenes and separate sets of glass apparatus were used for analysis.

The results of the oxidation series are given in Figs. 1–5 and by the sorptograms, Figs 6–8. Sorptograms of oxidized Δ^3-carene have been published earlier [6] and therefore have been excluded here. It is seen that Δ^3-carene is by far the most easily oxidized, α-pinene and (+)-limonene follow, with very similar behaviour, whereas β-pinene is very slowly oxidized and remains an easily flowing liquid when the others have become yellow resins. There is a relationship between the sorptograms due to degree of oxidation. The medical investigations show that the der-

* The oxidation series was performed in the period February to March, whereas the earlier reported [6] oxidation of Δ^3-carene was made during June and July. It is very likely that the slower rate in the present oxidation experiments is explained by the difference in illumination.

* The rate of oxidation has been corrected for this loss and the mole percent oxygen consumed has been calculated on the hydrocarbon remaining, assuming a monoreaction.

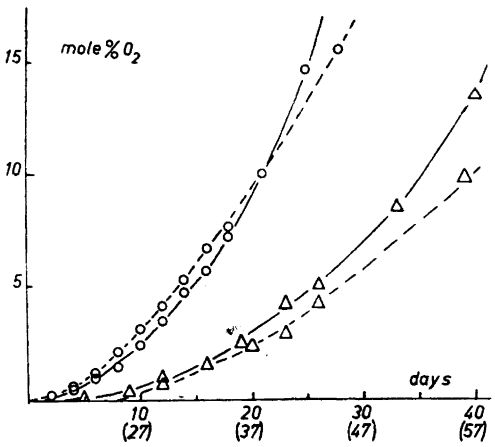

Fig. 2. Rates of oxidation of α-pinene (O) and β-pinene (△) and peroxide content. (β-pinene 18 to 50 days.)

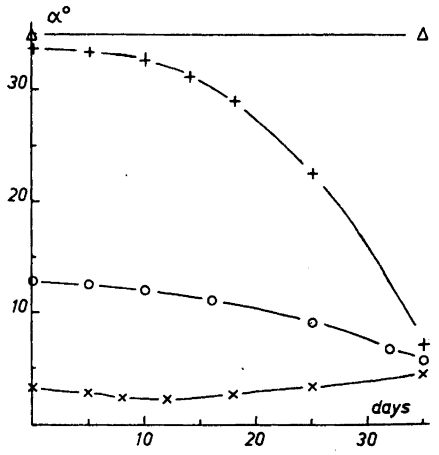

Fig. 4. Changes in optical rotations ($\alpha_{10\ cm}$); Δ^3-carene (pure) 15.°2, after 32 days 16.°4; α-pinene 29.°4 and 22.°8; β-pinene −18.°5 and −18.°5; (+)-limonene 102° and 70°, resp.

matologically active compounds are enriched in the "peaks" of the sorptograms. In the case of (+)-limonene a lift of the "plateau" in a sorptogram is observed.

This paper reports only the figures from the consumption of up to 20 mole percent of oxygen which from a dermatological and chemical point of view is the most interesting part. For the higher stages, the measurements become less accurate due to the marked increase in viscosity, and the curves are similar to that of Δ^3-carene previously reported by the present authors [6]. Furthermore, a detailed report together with the results of the medical investigation will be given elsewhere [8].

Experimental. The oxidation apparatus and the sorption equipment are similar to the ones used previously [6], but the surfaces of the oxidation vessels were made larger = 8.7—9.2 cm².

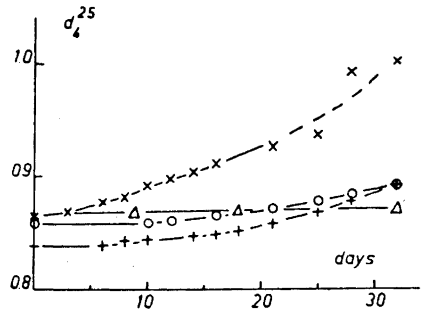

Fig. 3. Changes in densities during the oxidation. × = Δ^3-carene. O = α-pinene. △ = β-pinene. + = (+)-limonene. (The same marks are valid for Figs. 1—5.)

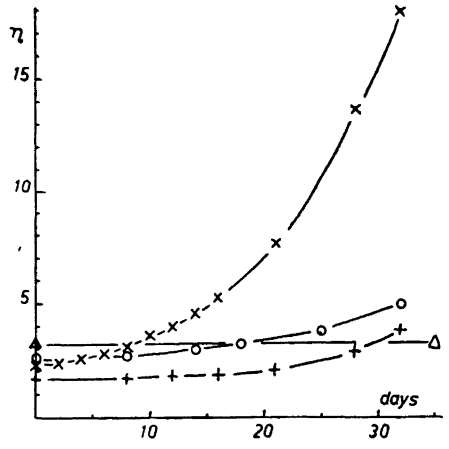

Fig. 5. Changes in viscosities, centipoises.

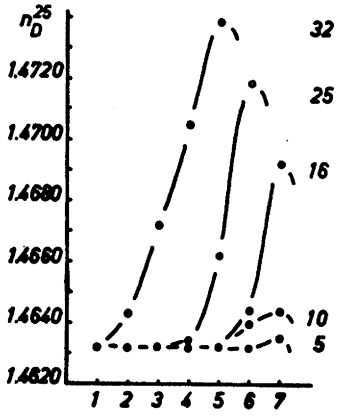

Fig. 6. Sorptograms of oxidized α-pinene. The number of days of reaction is given to the right.

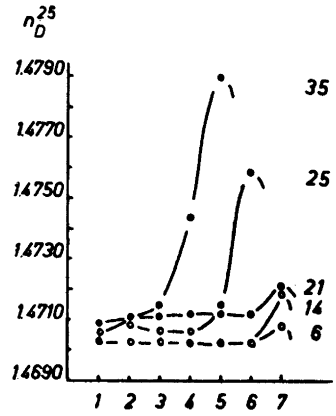

Fig. 8. Sorptograms of oxidized(+)-limonene.

The four viscometers, type Ostwald, volumes 3 ml, had the flow times for water at 25°C 16.9, 18.0, 15.3 and 15.2 sec. and the flow times of the pure terpenes (in the order given in the title) 24.1, 29.8, 30.6 and 16.4 sec., which gave 2.34, 2.66, 3.22 and 1.71 centipoises, respectively. The optical rotations were measured in four 10 cm tubes (volume 6 ml) which also have been used as containers when determining the densities by the aid of a Mohr's balance. In this case, a fall in the temperature of one degree was unavoidable. The iodine titrations were performed as before [6], but the time was increased to 12 min.

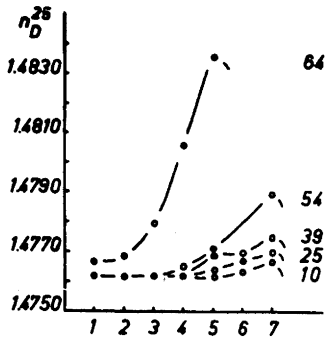

Fig. 7. Sorptograms of oxidized β-pinene.

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3. Widmark, G. and Blohm, S.-G. *Acta Chem. Scand.* **9** (1955) 1296.
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