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Ozonolysis as a Means to Study Putative Groups on the Polyisoprene Molecule

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The ozonolysis of deproteinised natural rubber or Natsyn 400 (a synthetic cis*-polyisoprene) and the subsequent reduction of the resultant ozonides led to the formation of 1,4-pentanediol and r-valerolactone. The storage hardening (crosslinking) of natural rubber has always been associated with reactions involving putative abnormal groups in the molecule. The understanding and the application of this ozonolysis and reductive procedure as discussed may be useful in determining and localising these groups on the rubber polymer.*

The controversy over the cause of storage hardening (crosslinking) in dry rubber has long been a subject of discussion. Sekhar[1], attributed the hardening process mainly to the aldehyde groups and their presence was empirically confirmed by Percy[2] and Subramaniam[3]. Other possible compounds include carboxylic[4,5] groups and lactones[6]. Burfield[7] proposed that the hardening of rubber on storage was due to a crosslinking reaction involving epoxide groups. Although many estimates of the number of aldehyde or other groups have been made[1,3,7], their exact locations on the rubber molecule are not known. Whether the rubber molecule contains a mixture of these groups or a single representative is also uncertain.

Being an unsaturated hydrocarbon, rubber is prone to attack and degradation by ozone. The mechanism of ozone attack and cleavage of the double bonds on rubber as postulated by Criegee[8] is reported to result in the formation of numerous five-carbon molecules or ozonides. Any group that is present in the initial rubber molecule should also be present as part of the ozonide after ozonolysis. The main product of oxidative hydrolysis of the ozonides as shown by McSweeney[9] was levulinic acid. This procedure was scarcely applicable to the detection of aldehyde or carboxyl groups in the rubber because of the difficulty in separating the abnormal reaction products from levulinic acid.

This paper presents results from preliminary work on the reduction of the ozonides of Natsyn 400 (a synthetic *cis*-polyisoprene) and deproteinised natural rubber (DPNR). The information gained should be useful in later investigation of the position of any abnormal groups in rubber from *Hevea* latex.

EXPERIMENTAL

Natsyn 400 and DPNR, 0.1 g, were each dissolved in a mixture of 15 ml AR chloroform and 5 ml ethanol. Ozonised oxygen generated by the Wallace and Tierman ozonator was bubbled into each of the solutions for 8.5 min at −30°C (150 ml O_2 min^{-1} at 150 V). The chloroform was evaporated with N_2 at room temperature. The remaining ozonide was reduced by 0.63 g $NaBH_4$ in 5 ml 50% aqueous ethanol at 50°C overnight. Concentrated HCl was added to each of the mixtures to decompose excess $NaBH_4$ and to precipitate the boric acid. The mixture was centrifuged and the supernatant collected and made alkaline with 0.5 *M* NaOH. The diol fraction was extracted into diethyl ether in a 50 ml separating funnerl, or by a liquid extraction method into chloroform.

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The aqueous layer was acidified and re-extracted with diethyl ether or chloroform to yield an acid fraction which was subsequently shown to contain γ-valerolactone. The approximate yield of purified diol was 850 mg and that of γ valerolactone was 0.10 milligramme.

Analysis of Diol Fraction

Gas-liquid chromatrographic analysis of diol. One microlitre of diol was injected into a 3.7 m x 6 mm GLC column (80% Carbowax 20 TPC on Chromosorb W 100-110 mesh) maintained at 22°C with N_2 as carrier gas flowing at 30 ml per minute.

Benzoylation of diol fraction with 4-nitrobenzoyl chloride. To the ether extract containing the diol fraction 0.3 g of 4-nitrobenzoyl chloride and 1 ml pyridine were added. The mixture was refluxed for 15 min and then evaporated to dryness; 10 ml of 0.1 *M* Na_2CO_3 solution was added to the residue and shaken vigorously. After filtering through a sintered funnel (Porosity No. 4), the residue was collected and dissolved in warm water. The 4-nitrobenzoate ester was dried under vacuum at 30°C overnight.

Nuclear magnetic resonance analysis of benzoylated diol. The NMR spectrum of the benzoate ester was determined in carbon deuterium trichloride ($CDCl_3$) solution using hexamethyl disilazane (HMDS) as internal standard at 0.05 part per million.

Analysis of Acid Fraction

Thin-layer chromatographic analysis of acid fraction. Ten microlitre of the acid was spotted on a silica gel (kieselgel GF 254 Type 60) plate, thickness 0.4 mm, and developed in chloroform: acetone (2:1, volume/volume).

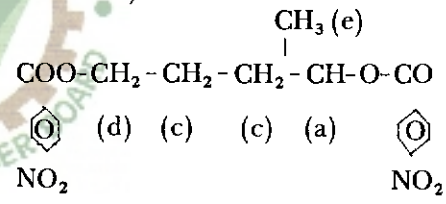
Gas-liquid chromatographic analysis of acid fraction. The acid fraction was analysed by GLC at 220°C using a similar column to that above.

RESULTS AND DISCUSSION

The diol, after passing through the GLC column had a retention time of 9 min which is identical to that of commercial 1, 4-pentanediol *(Figure 1)*. Nuclear magnetic resonance analysis of the benzoylated diol showed the following peaks:

Chemical shift (ppm)	Structure
8.2/8.3/8.4, 7.25/7.35(m)	8H aryl proton
5.3(m)	1H(a)-CH_2-$\underline{CH}$-OCO-
4.4(t)	2H(d)-CH_2-$\underline{CH_2}$-OCO-
1.9(m)	4H(c)-CH_2-$\underline{CH_2}$-CH_2-CH
1.42(d)	3H(e) $\underline{CH_3}$-CH

The above data is clearly in accord with the structure of 1,4-pentanediol di(nitrobenzoate):



The γ-valerolactone from the acid fraction detected as a black spot on the TLC plate had an *Rf* value of 0.56, after spraying the plate with hydroxylamine-ferric chloride reagent. The retention time for γ-valerolactone after passing through the GLC column was 6.2 min which was

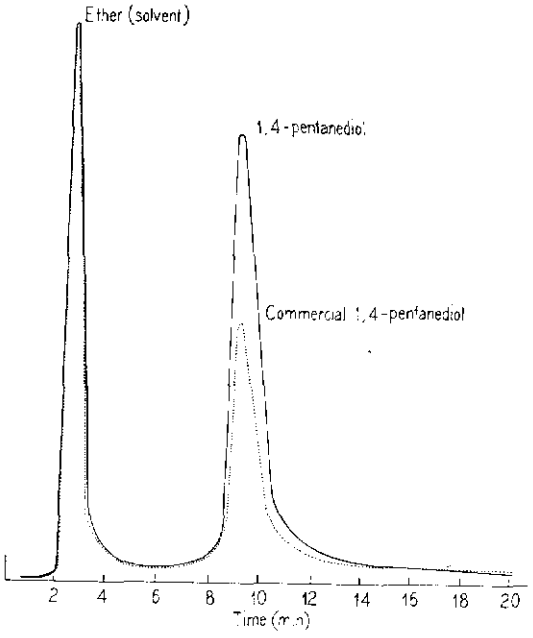


Figure 1. Gas-liquid chromatography of 1,4-pentanediol from the alkaline fraction of reduced cis-*polyisoprene ozonides. Commercial 1,4-pentanediol was used as standard.*

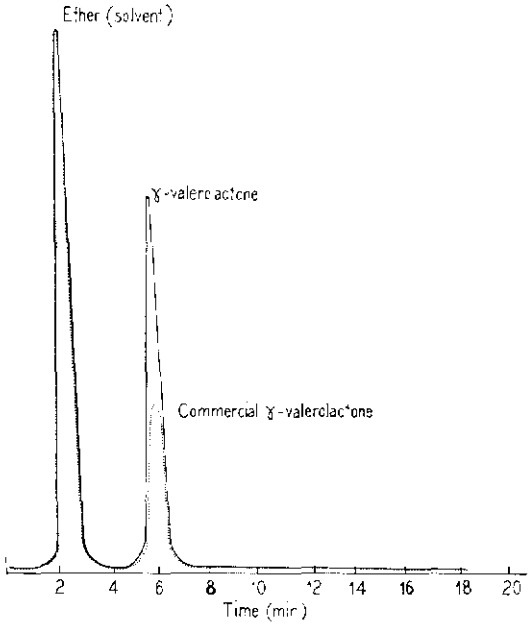


Figure 2. Gas-liquid chromatography of γ-valerolactone from the acid fraction of reduced cis-*polyisoprene ozonides. Commercial γ-valerolactone was used as standard.*

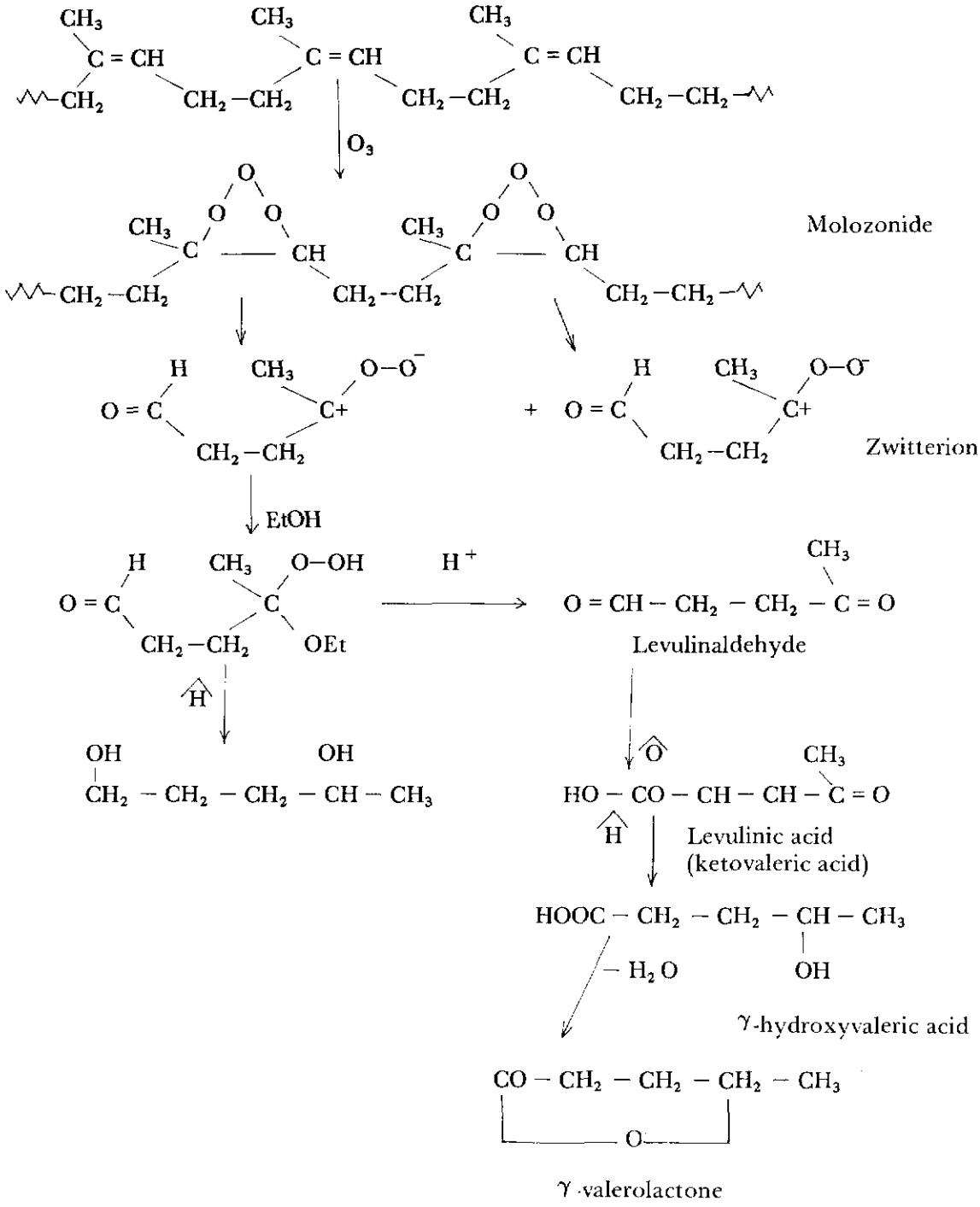
identical with that of a commercial standard *(Figure 2).*

The possible formation of 1,4-pentanediol and γ-valerolactone is summarised in *Reaction Scheme 1.*

Ozone, as stated earlier, reacts on the double bonds and cleaves them to form the unstable five-carbon molecules or zwitterions. In the presence of ethanol (EtOH) these zwitterions are converted to peroxide esters before being reduced by $NaBH_4$ to form 1,4-pentanediol. The function of EtOH is to stabilise the zwitterions and to reduce the formation of peroxide polymers.

The formation of γ-hydroxyvaleric acid is attributed to the reduction of levulinic acid formed in small amounts in the earlier stages of the reaction. Reduction of these compounds could result in γ-hydroxyvaleric acid. Under the prevailing conditions the γ-hydroxyvaleric acid lactonises to γ-valerolactone; $NaBH_4$ was used for its specificity towards reduction of aldehyde or carboxylic acid groups.

1,4-pentanediol and a smaller amount of γ-valerolactone as obtained from the synthetic cis-polyisoprene or DPNR should also be the main products when utilising the rubber from fresh *Hevea* latex. If abnormal groups (aldehyde, carboxylic,



Reaction Scheme 1

epoxide groups or lactones) are present on the rubber polymer, new compound(s) in addition to the above products may be formed.

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