

## Studies on Hydroperoxidation of Lac

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The effect of different variables on the extent of hydroperoxidation of bleached lac in aqueous and non-aqueous media in the presence and absence of added catalyst (potassium persulphate or benzoyl peroxide) has been investigated. The optimum conditions for obtaining maximum degree of hydroperoxidation in bleached lac are: conc. of lac, 20 per cent (wt/wt); conc. of potassium persulphate, 3.3 g./100 g. lac; and temperature, 50°C.

THE copolymerization of lac with acrylic acid esters in aqueous media has been the subject of study by several workers<sup>1,2</sup>. However, copolymers with outstanding film properties have been prepared only recently. One of the methods for copolymerization involves hydroperoxidation of lac and subsequent preparation of a graft polymer with vinyl monomers in the presence of a simple redox system<sup>1</sup>. In the present investigation lac hydroperoxide has been prepared in aqueous and non-aqueous media in the presence and absence of catalysts; the influence of various factors on the yield of the hydroperoxide has also been studied.

The auto-oxidation phenomenon is common in the reaction of organic compounds with oxygen under mild conditions. In a number of cases the hydroperoxide formed can itself act as an initiator, so that the reaction is autocatalysed. The initial abstraction of hydrogen from the hydrocarbon takes place more readily from a tertiary than from secondary or primary positions and hydrogen is readily removed from an allylic or benzylic position. Khurana *et al.*<sup>3</sup> studied the lac acids derived from *palas* seedlac [host tree: *palas*, *Butea monosperma* (Lamk) Taub.]. From a study of the composition of total lac acids, they concluded that the chief building blocks of the lac resin are aleuritic acid and jalaric acid-A. The structure of jalaric acid-A as an aldehydic acid (I) has been established by Wadia *et al.*<sup>4</sup>. According to them shellolic acid (III) and *epi*-shellolic acid are not the primary products of hydrolysis of lac resin, and these acids together with the two new acids described by them, laksholic and *epi*laksholic, arise from a Cannizzaro reaction of jalaric acid-A. This has been experimentally confirmed by subjecting pure jalaric acid-A to the base hydrolysis conditions and isolating all the four acids, which almost completely constituted the reaction product

Thus there is no doubt that the most important components of shellac are aleuritic acid, 9,10,16-tri-hydroxy palmitic acid and jalaric acid-A, a tricyclic sesquiterpene. These are connected most probably by lactide and ester linkages.

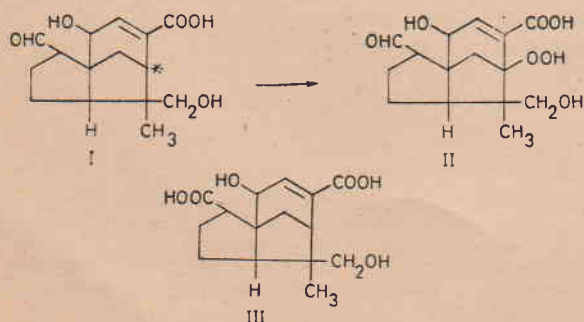
According to the above considerations the initial abstraction of hydrogen from jalaric acid-A can take place at the tertiary carbon atom marked with an asterisk, which is also incidentally an allylic position. The tentative structure of the hydroperoxide formed is thus (II).

To check the above hypothesis, the components, viz. aleuritic acid, jalaric acid-A and shellolic acid, were subjected to hydroperoxidation. Whereas aleuritic acid failed to yield the hydroperoxide as is warranted by its structure, both jalaric acid-A and shellolic acid could be hydroperoxidized, providing evidence that in shellac the vulnerable site for attack by oxygen is the tertiary carbon atom (\*) of jalaric acid-A

### Experimental Procedure

*Preparation of lac hydroperoxide in aqueous medium in the absence of added catalyst*—A solution of dewaxed bleached lac (25 g.) was prepared in a mixture of water (75 ml.) and aqueous ammonia (3 ml.) of density 0.91 by warming on a water bath to 60°C. The solution (50 ml.) was taken in a three-necked flask fitted with a water condenser, a mercury seal stirrer and a delivery tube for passing oxygen. The flask was immersed in a thermostatic bath maintained at 30°C. Oxygen gas (40-45 litres) was passed through the solution during 3 hr with constant stirring. The excess of oxygen was displaced by nitrogen during 30 min. The resulting solution was added to a large volume of acidulated water contained in a beaker. The precipitate obtained was filtered and washed several times with water until free from acid. The washed precipitate was first dried in air and then in a vacuum desiccator.

*Estimation of hydroperoxide*—Hydroperoxidized lac (7.5 g.) was dissolved in isopropyl alcohol and the volume made to 100 ml. Twenty-five ml. of this solution were transferred into a conical flask and sufficient isopropyl alcohol (10-15 ml.) added to the solution to keep lac from precipitation; this was followed by the addition of a saturated solution of potassium iodide (1 ml.) and glacial acetic acid (1 ml.). The mixture was then heated almost to boiling, kept at incipient boiling for about 5 min., with occasional swirling and without cooling, titrated



with standard 0.1N sodium thiosulphate to the disappearance of yellow colour. The hydroperoxide content was then calculated<sup>5,6</sup>, assuming the average molecular weight of bleached lac and bleached lac hydroperoxide to be 1000 and 1032 respectively.

*Preparation of lac hydroperoxide in aqueous medium in the presence of potassium persulphate as catalyst*—The experimental procedure used was essentially the same as above, except that potassium persulphate was added as a catalyst before passing oxygen.

*Preparation of lac hydroperoxide in non-aqueous medium in the absence of catalyst*—Bleached lac (10 g.) was dissolved in methyl ethyl ketone (40 g.). The solution was poured in a three-necked flask fitted with a water condenser and delivery tube and refluxed on a water bath. Oxygen gas (60 litres) was passed during 5 hr. The solution was then added dropwise in a large excess of water contained in a beaker with stirring. The precipitate was filtered and dried. The final drying was done in vacuum oven at 40°C. The hydroperoxide content was determined as above and found to be 2.42 moles of active oxygen per 100 moles of lac.

*Preparation of lac hydroperoxide in non-aqueous medium in the presence of benzoyl peroxide as catalyst*—The experimental procedure used was similar to the one employed earlier, except for the addition of benzoyl peroxide<sup>7</sup>. For the same quantity of lac as above (10 g.) and benzoyl peroxide (0.25 g.), the hydroperoxide content was determined and found to be 2.91 moles of active oxygen per 100 moles of lac.

*Hydroperoxidation of aleuritic acid*—The hydroperoxidation of aleuritic acid in aqueous medium in the absence of catalyst was done in a similar manner as for lac. The hydroperoxide content was found to be zero.

*Hydroperoxidation of jalaric acid-A and shellolic acid in the absence of catalyst*—These experiments were performed in non-aqueous media in the absence of catalyst as in the case of lac. After hydroperoxidation the solvent was evaporated to dryness under vacuum at 40°C. and the hydroperoxidized jalaric acid-A and shellolic acid were isolated as solids. The hydroperoxide contents for the hydroperoxidized jalaric acid-A and shellolic acid were found to be 0.86 and 0.95 moles of active oxygen per 100 moles of the acids respectively.

## Results and Discussion

The effects of different variables on the yield of lac hydroperoxide are evident from the results presented in Table 1. It is seen that the yield of hydroperoxide depends on temperature. The hydroperoxide formed from 20 per cent bleached lac solution is more than for the 25 per cent solution at all temperatures tried. For the 20 per cent solution the yield of hydroperoxide increases up to 50°C. and thereafter remains constant.

The yield of hydroperoxide also varies with the concentration of the catalyst (potassium persulphate). With 20 per cent concentration of bleached lac and temperature 50°C., the highest yield is obtained at potassium persulphate concentration 3.3 g./100 g. bleached lac. Further increase in catalyst concentration has no effect.

TABLE 1 — EFFECT OF DIFFERENT VARIABLES ON THE YIELD OF LAC HYDROPEROXIDE

Temp. °C.	Conc. of bleached lac %	Conc. of pot. persulphate g./100 g. lac	Hydroperoxide val.
27	20	0	0.86
40	20	0	0.86
50	20	0	1.03
60	20	0	1.03
70	20	0	1.03
80	20	0	1.03
50	10	3.3	3.60
50	15	3.3	3.71
50	20	3.3	3.81
50	25	3.3	1.54
50	20	0.66	2.42
50	20	2.00	3.20
50	20	2.66	3.63
50	20	3.33	3.81
50	20	4.66	3.81
50	20	6.66	3.81
50	20	3.3	3.81
60	20	3.3	2.93
70	20	3.3	2.42
80	20	3.3	2.06

With increase in the concentration of bleached lac in the solution at constant concentration of potassium persulphate (3.3 per cent) and temperature (50°C.), the yield of hydroperoxide goes on increasing with concentration up to 20 g. of bleached lac/100 g. of solution. With further increase in the concentration the yield of hydroperoxide falls.

With constant concentration of lac (20 per cent) and potassium persulphate (3.3 per cent) the yield of the hydroperoxide decreases with increase in temperature beyond 50°C. This is possibly due to the decrease in the half-life period of potassium persulphate occurring on increasing the temperature beyond 50°C. The observation finds support from the fact that the hydroperoxide formation depends on the duration of the reaction, the yield for 1, 2 and 3 hr reaction periods being in increasing order.

After hydroperoxidation, aleuritic acid did not give any hydroperoxide, indicating that there is no attack of oxygen molecules on any position of aleuritic acid under the particular conditions of hydroperoxidation. This is to be expected from the structure of aleuritic acid.

As the extent of hydroperoxidation of lac is low and the OH group and OOH group attached to the same compound give similar infrared spectra<sup>8,9</sup>, the infrared spectrum of lac hydroperoxide would be expected to be similar to that of lac. This was actually found true. The same would hold good for the hydroperoxides of jalaric acid-A and shellolic acid.

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