

SOME HITHERTO UNCHARACTERIZED LATEX POLYISOPRENES

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Abstract—Ten latex bearing Nigerian trees were screened for polyisoprenes: *Alstonia boonei*, *Landolphia owariensis*, *Chrysophyllum albidum*, *Ficus pumila*, *F. ovata*, *F. elastica*, *F. vogelli*, *Funtumia elastica*, *F. africana* and *Euphorbia pulcherima*. The relative yields of 1,4-polyisoprene are reported and compared with that of *Hevea brasiliensis*. Spectroscopic data as well as the viscosity average molecular weights are also given for these polyisoprenes.

INTRODUCTION

The literature is still scanty on many latex bearing tropical trees and shrubs even though a few of these plants have been exploited economically. *Hevea brasiliensis*, for example, is a good rubber source; the leaves and stems of some *Alstonia* species have found immense use in traditional medicine [1] while *Chrysophyllum albidum* is cherished for its fruit [2]. Some recent workers [3] isolated *cis*-1,4-polyisoprene from the latices of four *Landolphia* species (*L. owariensis*, *L. dulcis*, *L. dulcis* var. *bateri*, and *L. owariensis* var. *owariensis*) and gave the relative yields. In the present work, latices from ten tropical plants were investigated for their polyisoprene content and yields and properties related to that of *Hevea*.

RESULTS AND DISCUSSION

Rubber in the latex form is a high M_r polymer of isoprene. Polyisoprene can exist in different isomeric forms, with *cis*-1,4-isoprene, *trans*-1,4-isoprene, 3,4-isoprene, 1,2-isoprene, and cyclic units [4]. However, in the case of polyisoprene from the major plant sources, *Hevea* and *balata* (gutta-percha), a controversy exists as to the contribution of each isomeric form. For example, Binder [5, 6] suggests from infrared studies that *Hevea* and *balata* macromolecules contain 2.2 and 1.3% 3,4-units respectively. This view is not in agreement with the findings of Fraga [7] or Golub, *et al.* [8] who have shown that polyisoprenes from plant sources are essentially 100% 1,4-structures. Even among these 1,4-structures it is important to ascertain whether they are exclusively *cis* (or *trans*) or whether these polymers contain a small amount of the opposite isomer. In this work, I did not attempt to estimate the *cis/trans* ratios in the various 1,4-polyisoprenes.

The IR spectra of rubber from *Hevea* obtained in this work were in excellent agreement with those already reported by other workers [8, 9] and the spectra from the various latices gave a peak-to-peak match with this authentic spectrum. It was, thus, evident that the polymers are 1,4-polyisoprenes. Additionally, the ^1H NMR spectra also gave a peak-to-peak match, the resonances at 4.92τ , 8.00τ and 8.33τ corresponding to the trialkyl olefinic,

methylene and methyl proton absorptions respectively. The refractive indexes for the various polymers, n_D^{25} , were 1.5210 ± 0.0006 (lit. value, n_D^{20} 1.5218 for crepe rubber [10]). The viscosity average M_r , \bar{M}_v , of benzene solutions of the 1,4-polyisoprenes were calculated using the equation $(\eta) = k\bar{M}_v^a$, k and a are constants. Values of k and a , 5.02×10^{-4} and 0.667 respectively, reported in the lit. [11, 12] for natural rubber were used for these calculations. The results (Table 1) show that 1,4-polyisoprenes from these other latices have much lower viscosity average M_r , when compared with that of *Hevea brasiliensis*. Indeed, the M_r of *Hevea* rubber in cyclohexane solution by light-scattering technique reported elsewhere [13] was 1 300 000. The M_r values are, however, comparatively closer to that of *Balata* rubber which has been reported as 100 000 [13].

EXPERIMENTAL

Stem latices. The latex of each plant listed in Table 1 was collected by a knife tapping technique, as used for *Hevea brasiliensis*, from parts of Anambra State, Nigeria. The rubber latex from *Hevea brasiliensis* was, however, obtained from the Nigeria Rubber Board, Benin, Bendel State, Nigeria. The fresh latex sometimes contained solid contaminants from the stem particles. These were removed by filtration through a fine wire guaze. The density of each latex was determined before any coagulation could set in.

1,4-Polyisoprene content. 50 cm^3 of latex was diluted with 10 cm^3 of H_2O . HOAc (HCO_2H served equally) was gradually added from a burette with stirring until the latex coagulated (pH 4.2-5.1). The coagulum was washed with H_2O , dried and weighed before being dissolved in a beaker (60 cm^3) of C_6H_6 (300 cm^3). $(\text{C}_6\text{H}_5)_2\text{NH}$ antioxidant was added (1-2 parts of antioxidant to 100 parts of dried coagulum). This was titrated with Me_2CO from a burette until the solution became turbid. This addition was continued dropwise until a clear supernatant was produced along with pptd polymer. Sufficient time was allowed for the beaker contents to settle after which separation was effected by decanting the supernatant. This supernatant was titrated with more Me_2CO until no more polymer was obtained. The combined yield was washed with a generous amount of H_2O and dried in a vacuum oven.

Table 1. Some properties of 1,4-polyisoprenes (1,4-p) from plant latices

Latex from:	Family	Average latex density (g/cm ³)	% yield ⁺⁺ of 1,4-p (w/v)	(η) ^b	\bar{M}_v^b
<i>Alstonia boonei</i> De Wild	*	1.00	15.5	0.90	75 000
<i>Landolphia owariensis</i> Beauv	*	0.96	24.2	0.94	80 000
<i>Funtumia elastica</i> Preuss	*	1.00	30.0	0.91	77 000
<i>Funtumia africana</i> (Benth) Starf	*	1.00	19.0	0.85	69 500
<i>Chrysophyllum albidum</i> Don	**	0.96	22.1	0.82	66 000
<i>Ficus pumila</i> L.	***	1.00	14.7	0.60	41 000
<i>Ficus ovata</i> Vahl	***	1.00	20.4	0.83	67 000
<i>Ficus elastica</i> Roxb	***	1.00	24.8	0.92	78 000
<i>Ficus vogelli</i> miq	***	0.99	28.1	0.77	60 000
<i>Euphorbia pulcherrima</i> Wild ex Klotzsch	+	1.00	35.1	1.28	128 000
<i>Hevea brasiliensis</i>	+	0.98	44.3	5.37	1 100 000

*: Apocynaceae; **: Sapotaceae; ***: Moraceae; +: Euphorbiaceae; ++: average of 10 different results for each species; (η)^b: intrinsic viscosity (benzene solvent); \bar{M}_v^b = Viscosity average M_v based on (η)^b.

The polymer; 1,4-polyisoprene. Each polymer sample was consistent with the following spectral results: T60 ¹H NMR spectra, C₆H₆ solvent, int. TMS ref.: 4.92 τ , 8.00 τ , and 8.33 τ . IR ν_{max} cm⁻¹ (intensity: v=very, s=strong, m=medium, w=weak): 3030 (m), 2940 (vs), 2730 (vw), 1710 (w), 1670 (m), 1460 (vs), 1379 (vs), 1310 (w), 1240 (w), 1130 (w), 1085 (m), 1040-930 (w), 885 (w) 838 (s), and 750 (vw). Refractive indices were n_D^{25} 1.5210 \pm 0.006 (Abbe's). Viscosity average M_v , Table 1, were determined by conventional procedures using a suitable Cannon-Fenske viscometer.

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