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COMPARATIVE YIELD OF *CIS*-1,4-POLYISOPRENE FROM STEM LATEX OF FOUR *LANDOLPHIA* SPECIES

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Key Word Index—*Landolphia* species; Apocynaceae; natural *cis*-1,4-polyisoprene; rubber.

Abstract—The latex of a tropical liane, *Landolphia owariensis*, was coagulated with acetic acid. The dried coagulum was dissolved in benzene, the clear solution was decanted, when precipitation with acetone gave a polymer shown by IR and NMR spectroscopy to be *cis*-1,4-polyisoprene rubber. Similar investigations on three other *Landolphia* species were made to determine the relative yields of this natural *cis*-1,4-polyisoprene.

INTRODUCTION

Most *Landolphia* species are lianes [1] found growing wild in the tropical and subtropical rain forest regions of Africa. When a cut is made on the stem a milky-white, latex drips out copiously. Left without further treatment the bulk of this latex soon congeals to a dark-brown tacky extensible material. *Landolphia* rubbers are well known, but it is interesting that they consist only of *cis*-1,4-polyisoprene. The content of *cis*-1,4-polyisoprene in the latices of four *Landolphia* species is reported in this work.

RESULTS AND DISCUSSION

The coagulation method for the estimation of the crude dry rubber content (CDRC) depends on the pH of the medium. The work on *Hevea* [2] has shown that natural latex contains stabilizing proteins. Acetic acid denatures these proteins and this causes agglomeration of the rubber particles. TLC of the crude polymer A from *Landolphia* suggested one component, R_f 0.65, while the sooty flame of an ignition test indicated unsaturation. Like other natural rubbers [3], polymer A was readily autooxidized in air to resinous products. The refractive index, 1.5158 at 27°, compares favourably with the literature value, n_D^{20} of raw rubber, which is 1.5195 for smoked sheet and 1.5218 for creps [4].

The IR spectrum shows a peak-to-peak match with the reported spectrum of *Hevea* [5, 6] which has been shown to be natural *cis*-1,4-polyisoprene rubber [7, 8]. The spectrum rules out the *trans*-1,4-isomer which has sharp bands at 883, 862, and 801 cm^{-1} [8] and the 3,4-isomer characterized by absorptions at 566, 890 and 1760 cm^{-1} [7]. The ^1H NMR spectrum also confirms *cis*-1,4-polyisoprene. The peaks at 4.92 τ, 8.00 τ, and 8.34 τ, are the vinyl, methylene, and methyl proton absorptions respectively. This spectrum eliminates the occurrence of the *trans*-1,4-isomer with methyl absorptions at 8.40 τ [3, 9] and the 3,4-isomer with resonance at 5.33 τ due to the olefinic methylene protons [9].

Table 1 shows that 100 ml each of *Landolphia owariensis* and *Landolphia owariensis* var. *owariensis* yielded 24.20 and 23.35% respectively of natural *cis*-1,4-polyisoprene. *Landolphia owariensis* is thus a better rubber adulterant than the *L. owariensis* var. *owariensis* species. The figures for *Landolphia dulcis* and *Landolphia dulcis* var. *barteri* are 16.08 and 17.44% respectively.

EXPERIMENTAL

Stem latex. The latex used for these studies were collected by a knife tapping method as used for *Hevea brasiliensis* from four *Landolphia* species—*owariensis*, *dulcis*, *dulcis* var. *barteri* and *owariensis* var. *owariensis*—found in Imo and Anambra States of Nigeria. For each species, twenty different plants from different localities were investigated.

Estimation of the crude dry rubber content (CDRC). Clean undiluted latex (100 ml) was weighed and diluted with 20 ml water. HOAc was added gradually with vigorous stirring until there was coagulation of the latex (pH 4.2–5.1). The coagulum (Crude Dry Rubber, CDR) was removed, washed with water, dried, weighed, and used without further treatment in the next stage.

Precipitating cis-1,4-*polyisoprene from the CDR*. To a soln of the CDR in C_6H_6 (250 ml), $(C_6H_5)_2NH$ antioxidant (1–2 parts of the antioxidant to 100 parts of the CDR) was added, followed by the gradual addition, with stirring, of Me_2CO until the soln became turbid. The addition of Me_2CO was continued dropwise until the addition of one drop followed by vigorous stirring produced a clear soln with precipitation of polymer. The soln was kept for 2 hr to settle after which the precipitated polymer, A, was separated by decanting the supernatant. The Me_2CO treatment was repeated with the supernatant until no more A was obtained. The combined yield of A, which was later shown to be *cis*-1,4-polyisoprene rubber, was weighed after drying in a desiccator for percentage yield calculation (Table 1).

Substance A. ^1H NMR spectral results (internal TMS): 4.92 τ, 8.00 τ, and 8.34 τ (vinyl, methylene, and methyl proton absorptions respectively): 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); TLC R_f 0.65, Si gel (G Type 60, Merck) plates (20 cm × 5 cm × 0.25 mm) using petrol, $CHCl_3$–petrol (4:1) and I_2 vapour for detection; refractive index n_D^{27} 1.5158 (Abbe's).

Table 1. Percentage yield of *cis*-1,4-polyisoprene (*cis*-1,4-p) from 100 ml of stem latex

		L. owariensis	*L. dulcis*	*L. dulcis* var. *barteri*	*L. owariensis* var. *owariensis*
Average wt of latex (g/100 ml)		96.29	90.86	92.15	95.10
Wt of *cis*-1,4-p*:	1	23.19	14.52	16.08	22.20
	2	23.10	14.56	16.07	22.20
	3	22.80	14.88	16.01	22.21
	4	22.94	14.90	16.08	21.98
	5	22.90	15.02	16.08	22.06
	6	23.03	15.02	16.06	21.98
	7	24.03	14.46	16.10	22.41
	8	23.11	14.47	16.11	22.50
	9	22.94	14.48	16.10	22.24
	10	23.26	14.64	16.12	22.26
	11	23.38	14.20	16.15	22.18
	12	23.30	14.66	16.04	22.26
	13	23.30	14.35	16.04	22.16
	14	23.67	14.60	16.07	22.18
	15	23.62	14.61	16.10	22.21
	16	23.18	14'62	16.07	22.22
	17	23.12	14.43	16.02	22.19
	18	23.12	14.20	16.02	22.46
	19	24.00	14.68	16.06	22.15
	20	24.10	14.80	16.02	22.25
Average wt of *cis*-1,4-p		23.30	14.61	16.07	22.21
% yield of *cis*-1,4-p		24.20	16.08	17.44	23.35

*Twenty different plants of each species were investigated.

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