Indian Sapota Tree Rubber

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The sapota or sapodilla tree (botanical name: *Achras zapota* of sapotaceae family) grows in regions of the tropical and subtropical climates in south, west, and east India.¹ The Indian sapota tree is about half the size of the original South or Central American species which may grow to an average height of about 15 m.² The American plant exudes milky latex when the bark of the trunk is cut while the Indian plant is mostly dry. However, when the fruit of the Indian plant is plucked from its calyx, a milky latex oozes out.

The existence of both *cis* and *trans* polyisoprenes (chicle) in significant proportions is rare in rubber bearing plants and generally only one isomer is produced. The ratio of the *trans* and *cis* polyisoprenes in American sapota chicle rubber is reported^{3,4} to be between 2 and 3.5. The main objective of the present communication is to determine the ratio of *cis* and *trans* polyisoprenes in the Indian sapota rubber from ¹H and ¹³C nuclear magnetic resonance (NMR) and x-ray diffraction (XRD) data; no studies on XRD are available on sapota rubber.

EXPERIMENTAL

The latex from the sapota tree (Bangalore, age 40 years) was obtained by plucking the fruit from its calyx; it was collected in distilled water; the resin was extracted with benzene and purified by repeated precipitation with acetone. The crystalline product was separated by a centrifuge and dried in vacuum.

The ¹H NMR spectra were taken with a 60 MHz Varian T-60 spectrometer operating at ambient temperature with 1% (w/v) solution in CDCl₃ and tetramethylsilane (TMS) as the internal standard. The 67.89-MHz ¹³C NMR studies were performed on the Bruker WH-270 FT spectrometer at room temperature using a 2% (w/v) solutions in CDCl₃. Chemical shifts were referred to TMS. Both proton decoupled and off-resonance spectra were recorded. The XRD pattern of the sample was recorded with a Philips PW 1050/70 vertical Goniometer with nickel-filtered CuK α radiation generated at 30 KV and 20 mA.

RESULTS AND DISCUSSION

The absorption peaks in ¹H NMR (Fig. 1) at 5.08 δ , 2.00 δ , and 1.67 δ were assigned to the olefinic =CH, aliphatic —CH₂, and isoprenyl —CH₃ groups, respectively, which corresponded to *cis*-1,4-polyisoprene (PIP) from Hevea natural rubber (NR). An intense peak at 1.60 δ also appeared which corresponded to *trans*-PIP; the natural form is known as balata or gutta percha. This indicated that Indian sapota rubber contains both *cis* and *trans* PIP.

The proton decoupled ¹³C NMR showed ten absorption peaks, 135.27, 125.21, 32.34, 26.53, and 23.42 ppm for *cis* and 134.98, 124.47, 39.84, 26.89, and 16.06 ppm for *trans*-PIP, respectively. The chemical shift values (Table I, Fig. 2a) are very similar to the chicle rubber reported by Tanaka and Sato.⁵ General *cis* or *trans* structure of PIP is as follows.

Fig. 1. 60 MHz ^1H NMR of Indian sapota rubber.

The nature of the different carbon atoms present in the sapota rubber were confirmed from the off-resonance ^{13}C NMR spectra (Fig. 2b) which exhibited a singlet for C_2 , doublet for C_3 , quartet for C_5 , and triplet for C_1 for both cis and trans units. C_4 occurs as sextet (magnified spectrum shown in Fig. 2b) as the triplets of both cis and trans form intermingled due to the small difference in the peak region. The off

TABLE I
 ^{13}C NMR Data of Indian Sapota Rubber

Cis/trans-1,4-PIP

Chemical Shift (ppm)	Characteristic C-atom	peak intensity	Percentage intensity of (c) and (t)
135.27	C_2 (c)	7.63	22.3
134.98	C_2 (t)	26.63	77.7
125.21	C_3 (c)	17.51	23.0
124.47	C_3 (t)	58.67	77.0
32.34	C_1 (c)	15.22	20.8
39.86	C_1 (t)	57.87	79.2
26.53	C_4 (c)	17.43	26.6
26.89	C_4 (t)	57.20	73.4
23.42	C_5 (c)	12.30	27.4
16.06	C_5 (t)	32.65	72.6

(c) cis.

(t) trans.

Fig. 2. 67.89 MHz ^{13}C NMR spectrum of Indian sapota rubber (a) proton decoupled, (b) off-resonance.

resonance thus shows that C_2 is quaternary, C_3 is tertiary, C_2 and C_4 are secondary, and C_5 is primary in nature. This is in agreement with the general cis and trans structure of PIP.

The percentage of the trans to the cis isomer was calculated from the area of the ^1H NMR peak at 1.60δ and 1.67δ , respectively, and was found to be 2.8. The ^{13}C NMR peak intensities of different carbon atoms corresponding to cis and trans units are given in Table I from which the trans to cis ratio was found to be 3.0. Figure 3 shows the number of XRD peaks at 2θ values of 11.6° , 18.4° , 19.6° , 22.4° , 23.0° , 25.6° , 27.0° , 30.8° , 33.4° , and 43.0° . From XRD data the crystallinity pertaining to the trans isomer was determined adopting Hermans assumption⁶ with a regular region of $5\text{--}45^\circ$ (2θ) which corresponded to the trans to cis ratio of 2.46. The trans to cis PIP ratio in Indian sapota rubber as obtained by ^1H NMR, ^{13}C NMR, and XRD may be assigned to be between 2.5 to 3.0 which may be considered similar to that of American sapota rubber.

Sometimes 3,4-polyisoprene may also exist in small quantities along with cis and trans 1,4-PIP as reported by Stavely et al.⁴ in chicle rubber. However, in Indian sapota rubber this seems to be absent since it does not show any characteristic peak at 4.6δ in ^1H NMR^{7,8} nor any additional peak in ^{13}C NMR. This seems to be a unique feature of Indian sapota rubber.

Due to high temperature and well-distributed annual rainfall, the hot-wet equatorial climate of Central and South America supports luxuriant vegetation; the

Fig. 3. X-ray spectrum of Indian sapota rubber.

plants struggle upwards for sunlight resulting in taller trees. The tropical monsoon climate of India, with precipitation concentrated within a brief summer period of four months, supports less luxuriant vegetation of deciduous trees. This may be the reason for the much smaller size of the Indian trees. Low latex yields in the Indian sapota tree compared to its American counterpart may be attributed to the difference in climatic conditions similar to the variations observed in *Hevea* plants.^{9,10}

The cis-trans ratio in chicle is likely to depend mostly on temperature. The average temperature of central and peninsular India and that of Central and South America is between 27–32°C. For this reason, the trans to cis ratio in sapota rubber at these two places does not show much variation.

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