Valorisation of the Argan fruit pulp: a source of latex?

Argan Tree (Argania spinosa, Sapotaceae family), adapted to harsh environment, heat, drought and poor soil, and endemic of South-West Morocco, is a source of forage for goats, of high-value oil, and of firewood. The Argan oil is extracted from the nut, while the pulp contains a latex as do 2,000 species producing natural rubber: polysisoprene having a cis 1,4 (Hevea, Parthenium argentatum, Taraxacum kok Saglez) or a trans 1,4 stereoregular structure (gutta percha). Battino (1929) was the first to isolate latex from Argan pulp and showed it was a trans-isomer. Sandret (1957) found that this latex contains rubber at a concentration of 0.11% to 0.48% (fresh weight). Fellali-Zamrak et al. (1987) have shown that this polysisoprene of the Argan pulp can be either of the cis and trans structure, but that cis was prominent. Within the project RARCA PROD 2,IRAD and Agropolis have studied the valorisation of the Argan pulp, especially the rubber fraction.

**FTIR analysis**

- $\text{C}=\text{O}$ at 1735-1750 cm$^{-1}$ (fatty acid ester and protein carboxyl groups).
- $\text{C}=$ at 1626-1690 cm$^{-1}$ (polysisoprene and lipids).
- $\text{C}=$ at 800 et 840 cm$^{-1}$ cis polysisoprene.
- $\text{C}=$ at 2850-3000 cm$^{-1}$ and 1370-1470 cm$^{-1}$.

**NMR $^1$H analysis**

- $\triangleq \text{CH}_2$ (C$_{C_0}$ 1.63 ppm for cis 1,4 and $\triangleq \text{CH}_2$ 1.55 ppm for trans 1,4 stereoisomer.
- $\triangleq \text{CH}$ (C$_{C_0}$ 0.8-1.0 ppm and $\triangleq \text{CH}_2$ C$_{C_1}$ or C$_{C_2}$ 1.2-2.0 ppm and small peaks above 2 ppm belongs to long chains of saturated lipids and not to polysisoprene.
- For pure polysisoprene, total integration of all aliphatic groups below 2.5 ppm should be 7 times the peak at 5.5 ppm of CH (C$_{C_0}$) but it varies from 13 to 23 times, this confirms the presence of lipids.

**Co-existence of the cis and trans isomers respectively.**

**NMR $^{13}$C analysis**

- $\triangleq \text{CH}_2$ at 23-30 ppm is characteristic of lipid chains (confirmed by FTIR band 1733 cm$^{-1}$).
- $\triangleq \text{C}_0$ at 113 ppm and $\triangleq \text{C}_1$ at 125 ppm is characteristic of a polysisoprene.
- $\triangleq \text{CH}_2$ 12.2 ppm and $\triangleq \text{CH}_3$ C$_{C_1}$ at 39.8 ppm is a cis and trans respectively.

**Arrgania spinosa syntheseths the two forms of isomers of polysisoprene cis 1,4 and trans 1,4. Sapotaceae species are generally trans.**

**DSC analysis**

- Melting point (Tm) between 54-61°C corresponding to a trans 1,4 polysisoprene (gutta percha).
- Glass transition temperature (Tg) between -54°C and -65°C for cis 1,4 polysisoprene.

**SEC-MAL analysis**

- Polysisoprene of argan pulp has low molar mass between 58,000 and 143,000 g/mole (fig. 1). The Mw is much lower than hevea rubber (1 to $2.5 \times 10^6$) or guayule rubber (6 to $9 \times 10^5$).

**Conclusion**

- The rubber of Argan pulp contains the two polysisoprene isomers, cis 1,4 and trans 1,4, while rubber from Sapotaceae sp. (Gutta percha, Balatata) is mainly trans 1,4 polysisoprene, and Asteraceae (Hevea, Guayule) contains only cis polysisoprene.
- $^1$H and $^{13}$C NMR and FTIR spectra show contamination of rubber extracts by long chains of lipids which explains the high percentage of 1,4 cis=C=C bonds, but not from polysisoprene.
- DSC confirms trans isomer.
- The average molar mass (Mw) of Argan rubber is much lower than that of Hevea and Guayule.
- This potential source of rubber should find applications, based on its peculiar composition.

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**Fig. 1: Molar mass distribution for rubber from Argan, Hevea and Guayule analyzed by size exclusion chromatography coupled to a multangular right scattering detector (SEC-MALS).**

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