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THE EXISTENCE AND PHOTOCHEMICAL INITIATION OF FREE RADICALS IN *HYMENAEA* TRUNK RESIN

ALAN CUNNINGHAM*, PAUL R. WEST*†, GEORGE S. HAMMOND* and JEAN H. LANGENHEIM*

* Division of Natural Sciences, University of California, Santa Cruz, CA 95064 U.S.A. † University of Victoria, BC V8W 2Y2, Canada

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Key Word Index—*Hymenaea verrucosa*; Leguminosae; resin; resin polymer; amber; free radical; photoinitiation.

Hymenaea verrucosa Gaertn. (recently returned from *Trachylobium verrucosum* Gaertn. (Ol/iv) [1] trunk resin (J. H. Langenheim No. 5521) was collected from rainforest trees in the Kwale district of Kenya, Africa. Oligo-Miocene amber (fossil resin) (J. H. Langenheim No. B8413) which originally was derived from trunk resins of *Hymenaea* was collected near Simojovel, Chiapas, Mexico [2, 3]. Specimens documenting these collections are deposited at the University of California, Berkeley and Santa Cruz. Trunk resins known in the trade as 'copals' have been used for their toughness and durability for varnishes, paints and lacquers. They are also used in linoleums, paper sizing and for sealers [4, 5]. Amber is used for jewelery and high grade varnishes [3]. Earlier work on other species of *Hymenaea* [6] has been carried out on the trunk resin chemistry [4, 7–12]. The chemistry of the trunk resin of *H. verrucosa* has also been examined [8, 12]. We now report on the hardened trunk resin of *Hymenaea verrucosa* polymer isolated from the trunk resin of *H. verrucosa* and on amber of *Hymenaea* origin.

Trunk resin is secreted by epithelial cells lining pockets in the cambial zone and collects in cavities produced by the lysigenous breakdown of these secretory cells [13]. Upon any opening of the bark tissue, the resin may exude to the exterior of the tree where it forms hardened masses that contain up to 90% polymeric material [9, 10]. The gradual loss of volatile components which act as natural plasticizers, together with increased cross linking and oxidation, contribute to the hardening and aging process that resins undergo with time. The point in this aging process when resin is considered to be fossilized has not been well defined and the concept of fossilization is variously used. Resins simply buried in the soil around a tree frequently are referred to in the commercial resin literature as 'subfossil' [3].

We have been studying natural polymerization mechanisms in *Hymenaea* trunk resin and here report the existence of free radicals in both hardened trunk resins from *H. verrucosa* and Chiapas amber. The ESR signals were broad and there was no discernable fine structure in either signal. No radical signals were observed in purified polymer isolated from the resin. When the resin was illuminated with monochromatic electromagnetic radiation at various wavelengths within the natural solar envelope [14], a growth of EPR signal was observed (in UV light <400 nm) but not with light in the visible region of the spectrum. Detectable signal intensity growth was recorded at 360 nm reaching a maximum at 320 nm as the wavelength was decreased. Under the same conditions of radiant flux, no growth of radical signals was observed in amber or in *H. verrucosa* polymer. The results seem to suggest the presence of a quinone–hydroquinone system in the nonpolymeric portion of the resin. The observed broad and structureless ESR signal could be attributed to an oxy radical, such as a semi-quinone (g 2.0038 to 2.0045) which possibly acts as an initiator for polymerization of unsaturated constituents of the resin.

Free radicals previously have been reported in the fresh oleoresin of *Pinus silvestris* and colophony [15]. At elevated temperatures the ESR signals disappeared but irradiation with visible light (xenon lamp) regenerated ESR signals which appear related to the photoinitiated oxidation of certain tricyclic diterpene acids 15, 16]. Because xenon lamps produce considerable spectral energy at 300 nm whereas direct sunlight, skylight and light transmitted through vegetation fall off to essentially zero before reaching 300 nm [14], we suspect that the methodology used by Lagercrantz [15] did not simulate natural conditions. His methodology possibly represents in part a contribution of a photochemical process which cannot occur within the natural solar envelope. An example would be excitation of simple carbonyl compounds follows by hydrogen abstraction from suitable hydrogen donors to produce radicals [17].

EXPERIMENTAL

ESR spectra were obtained on a Varian 4502 spectrometer. Samples were crushed into pieces that would fit into quartz cells with a 4 mm i.d. A Varian pitch standard (2.0025 g) was used to calibrate spectra. The g value for radicals in *H. verrucosa* resin was 2.0037 $\pm$ 0.0005 with a peak width of 48 Gauss. Chiapas amber radicals had a g value of 2.0039 $\pm$0.0005 with a peak width of 80 Gauss. Irradiation was achieved employing a 2 KW high pressure mercury arc source (PEK labs AH6) focused through a Bausch and Lomb model 33-86-07 grating monochrometer directly onto samples maintained in the EPR cavity. Response was achieved over illumination periods of 30 min.

Polymer was isolated by dissolving resin in a polar solvent such as EtOAc and precipitating polymer with *n*-hexane. *Hymenaea verrucosa* polymer exhibited a softening temp. of 170–177° (uncorr.)

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VELUTINIC ACID, A NEW FRIEDELANE DERIVATIVE FROM *XYLOSMA VELUTINA* (FLACOURTIACEAE)

P. T. OTTO CHANG, GEOFFREY A. CORDELL, HARRY H. S. FONG and NORMAN R. FARNSWORTH
Department of Pharmacognosy and Pharmacology, College of Pharmacy, University of Illinois at the Medical Center, Chicago, IL 60612, U.S.A.

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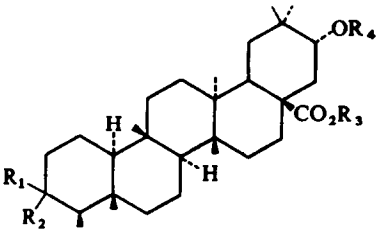
The pantropical genus *Xylosma* numbers in excess of one hundred species [1], but previous phytochemical [2] and pharmacological [3] work has been quite limited.

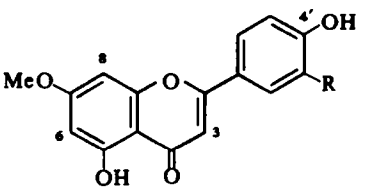
Chromatography of the chloroform soluble fraction from the twigs, leaves and inflorescence of *Xylosma velutina* afforded three pure components; two known flavonoids and a new triterpene acid.

Velutinic acid (1) crystallized from $CHCl_3$, mp 288–290°, and the physical and chemical data (see Experimental) indicated the presence of carboxyl, hydroxyl and ketone functions with a molecular weight of 472.

The general appearance of the MS fragmentation patterns of the substance and its derivatives, particularly the strong peak at *m/e* 273 in velutinic acid shifting to *m/e* 275 in the dihydro derivative, were consistent with the presence of a friedelane nucleus [5, 6]. From the fragmentation patterns of velutinic acid (1) and dihydrovelutinic acid (2), the ketone group could be located in ring A or ring B. There was no M^+-15 peak in the MS of velutinic acid; however significant peaks were observed at *m/e* 409 (M^+-H_2O − CO_2H) and 408 (M^+-H_2O − HCO_2H), and related fragments were also found in the MS of methyl velutinate (3) and acetyl methyl velutinate (4), indicating that there was a carboxyl group at position 17 [5]. The remaining functional group (hydroxyl) is situated in ring E of velutinic acid, as indicated by the mass shifts in the corresponding fragments of 1, 3 and 4.



1 R_1, R_2 = =O; R_3 = H; R_4 = H
2 R_1 = α-H; R_2 = β-OH; R_3 = H; R_4 = H
3 R_1, R_2 = =O; R_3 = Me; R_4 = H
4 R_1, R_2 = =O; R_3 = Me; R_4 = COMe
5 R_1 = α-H; R_2 = β-OH; R_3 = H; R_4 = COMe
6 R_1 = α-H; R_2 = β-OH; R_3 = Me; R_4 = COMe



7 R = OMe
8 R = H