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TERPENES FROM PITTOSPORACEAE

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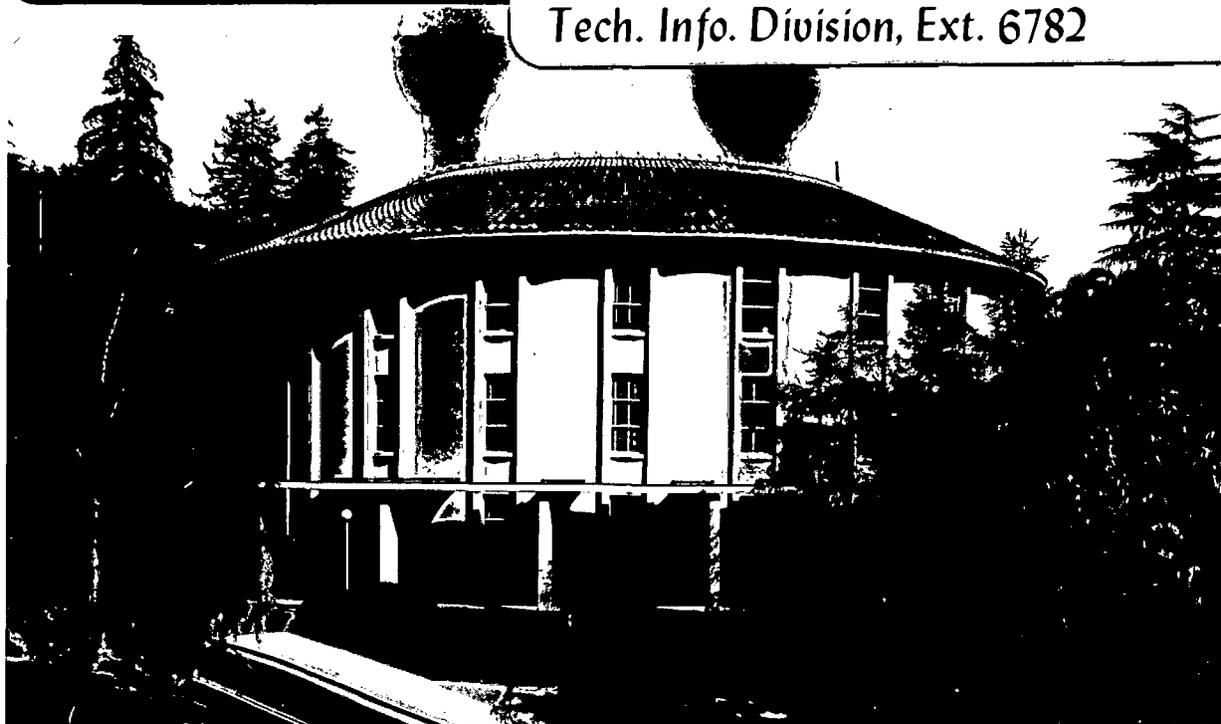
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TERPENES FROM PITTOSPORACEAE

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Key word index: Pittosporum resiniferum, Pittosporum undulatum, essential oil, monoterpenes, α -pinene; myrcene, limonene.

Abstract: The monoterpene constituents of the fruits of Pittosporum resiniferum and Pittosporum undulatum have been identified. The essential oil of Pittosporum resiniferum contains myrcene and α -pinene in equal quantities, whereas the major terpene constituent of Pittosporum undulatum oil is limonene.

This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Applications for Industry of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

The fruits of the tree Pittosporum resiniferum (family Pittosporaceae) have been reported to contain the unusual natural product n-heptane (Fernandez, E., personal communication). It is reported that even the green fresh fruit will burn brilliantly when a match is applied to it and that the expressed oil of the fruit is flammable. This species is native to the Philippines where the nuts are sometimes used as torch light [1]. Pittosporum fruit, therefore, shows promise as a potential alternate liquid energy source, and we have examined the chemical composition of this oil. The two alkanes n-heptane and n-nonane are minor components of this oil; the major components are two volatile monoterpenes, α -pinene and myrcene.

Another species of this family, Pittosporum undulatum, is widespread in California, and it produces small fragrant orange fruits in abundance. P. undulatum fruits were collected on the University of California Berkeley Campus during November and December 1981. The n-alkanes could not be detected in the oil of P. undulatum. Limonene is the only major monoterpene present in this oil, accounting for 99% of the monoterpene fraction; α -pinene is the minor component. No oxygenated monoterpenes were detected in either of these oils, but both contained minor quantities of sesquiterpene hydrocarbons.

A few members of the family Pittosporaceae have been subject to phytochemical investigation. Phytosterols have been isolated from the bark of P. floribundum [2], P. colensoi, and P. eugenoides [3]. Polyacetylenic compounds have been isolated from roots of P. buchanani [4], P. crassifolium, P. tobira and P. undulatum [5]. However, there are no prior reports on the essential oils of any Pittosporum species.

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Experimental:

Capillary GC analyses were obtained using either a 40 m SP2250 SCOT, an 80 m Carbowax 20M column, temp. programmed from 40^o to 200^o at 4^o/min. Where indicated, percentages refer to computer-calculated peak areas without correction to response. Preparatory GC was carried out on a 10' 4 mm ID 10% SP2250 glass column at 110^o. Coupled GC/MS were carried out on the SP2250 column interfaced to a Finnigan 4000 mass spectrometer at 70 eV. ¹H NMR spectra were recorded at 250 MHz in CDCl₃ with TMS as internal standard.

Analysis of P. resiniferum essential oil. Ripe fruits were homogenized in a Waring blender, then extracted with CH₂Cl₂ by stirring under N₂ at ambient temperature for 24 hrs. After slow distillation of the CH₂Cl₂ a light orange oil, 8-10% of the fr.wt. was obtained. GC/MS analysis of the oil indicated the presence of n-heptane (5%)*, n-nonane (7%), three isomeric monoterpenes (85%) and six minor sesquiterpenes (6%). The two major monoterpenes were isolated by preparative GC and identified as α-pinene (38%) and myrcene (40%) by ¹H NMR, MS and coelution with standards on the SP2250 and Carbowax 20M capillary columns. Catalytic hydrogenation of the oil (Pd on C, 1 atm) gave pinane and 2,6-dimethyl-octane, identified by MS and GC retention time.

α-pinene: ¹H NMR (250 MHz) δ 5.17 (1H,s), 2.33 (1H,m), 2.2 (2H, br.s), 2.18(1H,br.s), 1.94 (1H,m), 1.65 (3H,s), 1.26 (3H,s), 1.5 (2H,m), 0.83 (3H,s).

MS: m/z: 136, 121, 107, 105, 93 (b.p.), 79, 77.

Myrcene: ¹H NMR (250 MHz) δ 6.37 (1H,m; J = 10.7, 17.6 Hz), 5.4-4.9 (5H), 2.2 (4H,m), 1.7 (3H,s), 1.6 (3H,s).

MS: m/z: 136, 131, 107, 94, 93 (b.p.), 69, 41.

Analysis of P. undulatum essential oil. Fresh fruits were extracted in the same manner as before, but with petroleum ether. A light orange oil, 4-5% of the fresh fruit weight, was obtained. Chromatography on silica gel, eluting with petroleum ether, gave the hydrocarbon fraction which was 50% of the oil. GC and GC/MS analyses showed the presence of two monoterpenes in a ratio of 10:1, which coeluted with limonene and α -pinene, respectively. Limonene was purified by preparative GC and identified by ^1H NMR. Catalytic hydrogenation of the oil (Pd on C, 1 atm) gave 1-isopropyl-4-methylcyclohexane and pinane, identified by MS and GC retention times.

Limonene: ^1H NMR (250 MHz) δ 5.7 (1H,s), 4.7 (2H,s), 2.2-1.67 (5H,m), 1.67 (3H,s), 1.59 (3H,s), 1.47-1.4 (2H,m).

MS: m/z: 136, 121, 107, 93, 79, 68 (b.p.).

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* The % n-heptane may be too low, since some may have evaporated in transit.

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