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DITERPENES OF *PINUS QUADRIFOLIA*

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Key Word Index—*Pinus quadrifolia*; Pinaceae; strobic acid; new 8,15-isopimaradiene type diterpenes.

Plant. Pinus quadrifolia Parl. (Parry pinyon), MAD, MADw 25401. *Source.* Thomas Mountain, San Bernardino, Californio, U.S.A. *Previous work.* Wood.[1]

Wood. Small chips of mixed sapwood and heartwood were exhaustively extracted with Et_2O and the extract separated into an acidic fraction and a neutral fraction using DEAE-Sephadex.[2] The large proportion of Δ^8-isopimaric (8,15-isopimaradien-18-oic) acid caused difficulties in isolating an unidentified resin acid (which we suspected to be strobic acid[3a] based on GLC retention characteristics) by $AgNO_3$-silica column chromatography of the methyl esters. However, hydrogenation of the methylated (CH_2N_2) acidic fraction with a homogeneous catalyst before the $AgNO_3$ chromatography greatly enhances isolation of the methyl strobate.[3b] Thus, from Parry pinyon wood, we were able to isolate a pure sample of methyl strobate that by NMR and GLC[4] was identical with authentic material. The unidentified resin acid in Parry pinyon wood reported by Anderson *et al.*[1] is therefore shown to be strobic acid; however, our wood sample contained a much smaller proportion of the acid than that reported by those workers. We also isolated methyl strobate from the cortex tissue by preparative GLC of the methylated acids. The composition of the diterpene resin acids in the wood, cortex and needles was determined by GLC (DEGS)[4] and is shown in Table 1.

TABLE 1. COMPOSITION OF THE RESIN ACID FRACTIONS OF PARRY PINYON

Resin acid*	Wood (%)	Cortex (%)	Needles (%)
Δ^8-Isopimaric	75	61	82
Isopimaric	6	18	5
Strobic	1	11	6

* Pimaric, sandaracopimaric, levopimaric/palustric, abietic, dehydroabietic and neoabietic acids were also present in small amounts.

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* Maintained in cooperation with the University of Wisconsin.

[1] ANDERSON, A. B., RIFFER, R. and WONG, A. (1970) *Holzforschung* **24**, 182.

[2] ZINKEL, D. F. and ROWE, J. W. (1964) *Anal. Chem.* **36**, 1160.

[3] (a) ZINKEL, D. F. and SPALDING, B. P. (1971) *Tetrahedron Letters* 2459; (b) ZINKEL, D. F. and SPALDING, B. P. (1973) *Tetrahedron* **29**, to be published.

[4] ZINKEL, D. F., ZANK, L. C. and WESOLOWSKI, M. F. (1971) TANAKA, O., MIHASHI, S., YANAGISAWA, I., NIKAIDO, T. and SHIBATA, S. (1972) *Tetrahedron* **28**, 4523, attribute the formation of norditerpene alcohols to oxidation of the diterpene alcohol. Forest Products Laboratory, U.S.D.A., Madison, Wis.

The non-saponifiable portion of the neutral fraction from the wood extract was chromatographed on silica, and separated into several fractions that were further purified by $AgNO_3$-silica chromatography and by preparative GLC when necessary. As expected, a series of compounds based on the 8,15-isopimaradiene skeleton was found. The following new, natural products were isolated and identified primarily by their NMR spectra[5] ($CDCl_3$): 8,15-isopimaradiene, δ 0·96, 0·96, 0·88 and 0·85 (four methyl singlets); 8,15-isopimaradien-18-al, δ 1·10, 1·03 and 0·98 (three methyl singlets) and 9·33 (CHO), $[\alpha]_D^{25}$ +108° (c 1·0, $CHCl_3$), crystals from pentane had an m.p. 31·5–32°; 8,15-isopimaradien-18-ol, δ 1·00, 0·97 and 0·80 (three methyl singlets) and an *AB* quartet ($\delta_A = 3{\cdot}18$, $\delta_B = 3{\cdot}43$; J 11 Hz); 18-norisopimara-8,15-dien-4-ol,[6] δ 1·16, 0·97 and 0·93 (methyls at C-4, C-13 and C-10, respectively); and 19-norisopimara-8,15-dien-4-ol,[6] δ 1·18, 1·12 and 0·97 (methyls at C-4, C-10 and C-13, respectively). In addition, a number of minor constituents were also found. Dehydroabietal and dehydroabietol were isolated and identified by NMR comparison with the authentic material; geranylgeraniol was identified by NMR, IR and GLC comparison with authentic material. Abietadiene, palustral and *trans*-communol were tentatively identified by NMR.

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[5] The NMR for all compounds showed the same vinyl pattern as methyl 8,15-isopimaradien-18-oate.[4] HALL, S. F. and OEHLSCHLAGER, A. C. (1972) *Tetrahedron* **28**, 3155 report NMR data for 8,15-isopimaradiene and other diterpene hydrocarbons.

[6] Assignments of the C-4 stereochemistry of the norisopimara-8,15-dien-4-ols are based on the relative shielding of the C-10 methyl by the tertiary alcohol. See ROWE, J. W., NAGASAMPAGI, B. A., BURGSTAHLER, A. W. and FITZSIMMONS, J. W. (1971) *Phytochemistry* **10**, 1647 for the nordehydroabietols and ROWE, J. W., RONALD, R. C. and NAGASAMPAGI, B. A. (1972) *Phytochemistry* **11**, 365 for the norpimar-8(14)-enols. CAPUTO, R., MANGONI, L., PREVITERA, L. and IACCARINO, R. (1971) *Tetrahedron Letters* 3731 have reported that large losses of diterpene aldehydes occur during chromatography on silica or alumina and suggest that norditerpene alcohols are formed as artifacts from the aldehydes. However, in our experience in the chromatography of a number of deterpene aldehydes on silica, we have not observed any significant losses. Diterpene Resin Acids. A Compilation of Infrared, Mass, Nuclear Magnetic Resonance, Ultra-violet Spectra and Gas Chromatographic Data (of the Methyl Esters).

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NEUTRAL TRITERPENES FROM THE GALLS OF *PISTACIA TEREBINTHUS*

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In a previous paper[1] we reported that the acidic fraction of the resin from the galls of *Pistacia terebinthus* is essentially a mixture of known masticadienonic[2] and isomastica-

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[1] CAPUTO, R. and MANGONI, L. (1970) *Gazz. Chim. Ital.* **100**, 317.

[2] BARTON, D. H. R. and SEOANE, E. (1956) *J. Chem. Soc.* 4150.