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STROBIC ACID, A NEW RESIN ACID
from *Pinus strobus*

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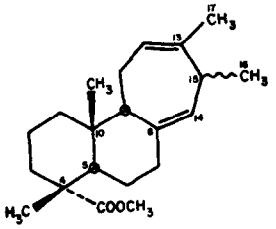
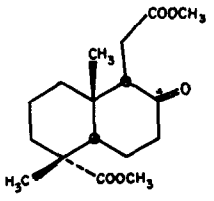
In 1967, Santamour (1) reported the occurrence of an unknown resin acid in the cortex oleoresin of eastern white pine (*Pinus strobus* L.). This acid, herein named strobic acid [14(13→15ξ)*abeo*pimara-8(14),12-dien-18-oic acid] (2), has now been isolated as its methyl ester and its structure has been established as I. This acid comprises 8-44% of the resin acids in the cortex oleoresin and 0-32% of the resin acids of the needle extract. The acid was not found, however, in the xylem of any of the trees examined. The occurrence of a seven-membered-ring resin acid and its distribution are particularly interesting from biosynthetic and taxonomic views.



I



II

Methyl strobate was isolated by column chromatography of the methylated (CH_2N_2) oleoresin on silver nitrate-alumina. Elution with 3:7 ether-petroleum ether yielded I in 99+% purity (established by GLC): $[\alpha]_D^{23}$ -48.9°(*c* 2.8 $CHCl_3$); mass spectrum m/e 316 (100%, M^+), 301(27%, M^+-CH_3), 257(33%, $M^+-COOCH_3$), 241(21%, $M^+-CH_3-COOCH_3$) and 221(25%, $M^+-C_7H_{11}$); $\nu_{max}^{CCl_4,CS_2}$ 1730 (C=O) and 1245 cm^{-1} (equatorial carbomethoxy); $\lambda_{max}^{193.6}$(ε 15,400, isooctane); NMR ($CDCl_3$) δ 0.87 (s, C-10 methyl), 1.17 (d, J=7 Hz, C-15 methyl), 1.18 (s, C-4 methyl), 1.66 (s, C-13 methyl on double bond), 2.70 (m, one H at C-15), 3.63 (s, $COOCH_3$), 5.41 (t, J=7, one olefinic H) and

*Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

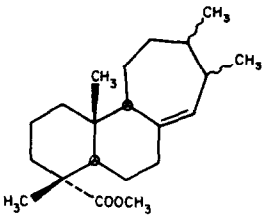
5.44 (d, J=7, one olefinic H). Double resonance experiments show that the δ 2.70 hydrogen is coupled to both the δ 1.17 methyl(d) and the δ 5.44 olefinic hydrogen. Based on the spectral data, structure I was proposed for methyl strobate.

A microscale isomerization of methyl strobate by heating with *p*-toluene sulfonic acid in benzene (16 hrs.) resulted in a crude mixture which showed a λ_{max}^{240} (ε 10,700); however, the mixture represented at least five major components as analyzed by GLC. Attempts to isomerize methyl strobate with NaOH in either ethylene glycol or ethanol failed to induce conjugation.

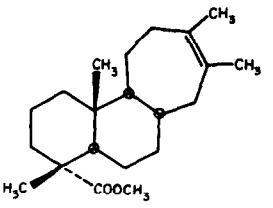
Methyl strobate was subjected to exhaustive ozonolysis, Jones oxidation, and methylation following the procedure of Pelletier *et al* (3) to yield a major product $[\alpha]_D^{25}$ -52.4°(*c* 1.9 $CHCl_3$) which was pure as shown by GLC and TLC. The NMR and IR spectra as well as the GLC and TLC retention characteristics were identical with those of the known keto diester II (3) $[\alpha]_D^{25}$ -50.7°(*c* 1.1, $CHCl_3$) which we prepared by the above procedure. Thus the double bond positions, the substituents on the A and B rings, and the stereochemistry at C-4, C-5, C-9, and C-10 are unambiguously assigned. The NMR data for the parent methyl strobate allow for only one arrangement of the carbon atoms in the (unstable) 5-carbon atom ozonolysis fragment.

Hydrogenation of methyl strobate in ethanol for 24 hrs. (1 atmos. 25°) over Adams catalyst yielded four major hydrogenation products: two tetrahydrostrobates and two dihydrostrobates. These products were purified by a combination of silver nitrate-alumina column chromatography and preparative GLC. The vicinal double bond methyl substitution of dihydrostrobate III (see below) confirms the relative location of the C-ring methyl groups. The mass spectra obtained for strobate, the dihydrostrobate III, and the tetrahydrostrobate V confirm the tricyclic and di-unsaturated nature of the parent methyl strobate.

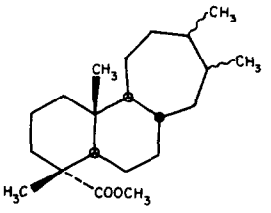
The stereochemistry at C-8 of the dihydrostrobate IV and the tetrahydrostrobates (V, VI) was assigned in analogy with observations on the tetrahydroabietates (4) and the tetrahydropimarates/tetrahydroisopimarates (5); *cis* BC ring junctions result in downfield shifts of the C-10 methyl hydrogens in the NMR spectra.



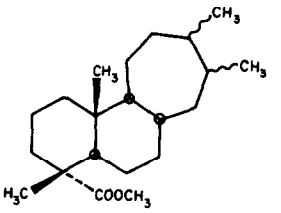
III



IV



V



VI

The physical and spectral data for the hydrogenation products are as follows:

14(13→15ξ)*abeo*-13ξ-pimar-8(14)-en-18-oate (III): NMR($CDCl_3$) δ 0.75 (d, J=7, C-13 methyl), 0.88 (s, C-10 methyl), 0.98 (d, J=6, C-15 methyl), 1.22 (s, C-4 methyl), 3.62 (s, $COOCH_3$) and 4.99 (d, J=6, one olefinic H); ν_{max}^{film} 1732, 1245 and 852 cm^{-1}; mass spectrum m/e 318 (17%, M^+), 303 (4%, M^+-CH_3), 259 (17%, $M^+-COOCH_3$), 243 (4%, $M^+-CH_3-COOCH_3$), 221 (2%, $M^+-C_7H_{13}$) and 121 (100%, $M^+-C_{12}H_{21}O_2$); $[\alpha]_D^{25}$ -8.6°(*c* 2.4, $CHCl_3$).

14(13→15)*abeo*-8α-pimar-13(15)-en-18-oate (IV): NMR($CDCl_3$) δ 0.99 (s, C-10 methyl), 1.17 (s, C-4 methyl), 1.57 and 1.60 (s, two methyls on double bond), 3.63 (s, $COOCH_3$); $\nu_{max}^{CCl_4,CS_2}$ 1730 and 1245 cm^{-1}; $[\alpha]_D^{25}$ -80.0°(*c* 1.3, $CHCl_3$); m.p. 105-107° corr. (evac. capillary).

14(13→15ξ)*abeo*-13ξ-pimaran-18-oate (V): NMR($CDCl_3$) δ 0.80 (s, C-10 methyl), *ca.* 0.88 (m, two methyls), 1.13 (s, C-4 methyl), 3.62 (s, $COOCH_3$); ν_{max}^{film} 1730 and 1245 cm^{-1}; mass spectrum m/e 320 (80%, M^+), 261 (58%, $M^+-COOCH_3$), 245 (10%, $M^+-CH_3-COOCH_3$), 163 (100%, $M^+-C_9H_{17}O_2$); $[\alpha]_D^{25}$ +8.1°(*c* 1.6, $CHCl_3$); m.p. 68.0-68.5° corr. (evac. capillary).

14(13→15ξ)*abeo*-8α,13ξ-pimaran-18-oate (VI): NMR($CDCl_3$) δ 0.79, 0.80 (d, two methyls), 0.96 (s, C-10 methyl), 1.17 (s, C-4 methyl) and 3.62 (s, $COOCH_3$); $\nu_{max}^{CCl_4,CS_2}$ 1730 and 1245 cm^{-1}; $[\alpha]_D^{25}$ -12.1°(*c* 1.1, $CHCl_3$): m.p. 72-73.5° corr. (evac. capillary).

Table I. GLC Retention Data for Methyl Strobate and Derivatives

Compound	r_{pim}*	
	DEGS	SE-30/EGiP
Methyl strobate (I)	1.74	1.39
dihydrostrobate (III)	1.39	1.31
dihydrostrobate (IV)	1.93	1.71
tetrahydrostrobate (V)	1.03	1.25
tetrahydrostrobate (VI)	1.39	1.56
keto diester (II)	8.03	1.00

*r_{pim} = Retention relative to methyl pimarate: for GLC conditions see (6).

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References:

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2. The systematic nomenclature follows the recent proposals of a committee chaired by Dr. J. W. Rowe, *The Common and Systematic Nomenclature of Cyclic Diterpenes*, Forest Products Laboratory, USDA, Madison, Wis., (1968; with Addenda and Corrigenda, February 1969).
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