TRICYCLIC NEUTRAL DITERPENOIDS FROM THE OLEORESIN OF Pinus koraiensis

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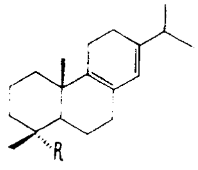
We have previously [1, 2] reported the isolation from the oleoresin of Pinus koraiensis (Korean pine) of eighteen neutral diterpenoids belonging to the structural-stereochemical groups of cembrane, labdane, and abietane. In the present communication we give information on eight more diterpenoids that have been isolated, five of which have the isopimarane carbon skeleton.

The chromatography of a mixture of the neutral substances of the oleoresins on alkaline alumina (activity grade II-III) gave fractions containing hydrocarbons (40%), carbonyl compounds (5%), monohydric alcohols (45%), and polyfunctional compounds (10%) (eluent: petroleum ether with increasing concentrations of diethyl ether). Rechromatography of the hydrocarbon fraction on SiO_2 + 5% $AgNO_3$ gave isopimara-7,15-diene with n_D^{24} 1.5168, $[\alpha]_D^{21}-29°$ (c 1.84; chloroform). Literature data [3]: $[\alpha]_D^{20}-31.3°$. Similarly, from the carbonyl-compound fraction we isolated: methyl isopimarate with mp 61-62°C (ethanol) $[\alpha]_D^{22}-7°$ (c 2.0; chloroform) (literature data [4]: mp 62.5°C, $[\alpha]_D-7.71°$);isopimarinal with $[\alpha]_D^{20}-13°$ (c 1.5; chloroform), 3,5-DNPH, mp 180-182°C (literature data [3]: $[\alpha]_D^{22}-15°$, 1,5-DMP, mp 182-183°C);isopimara-8(9),15-dien-18-al with $[\alpha]_D^{27}+80.8°$ (c 10.47; chloroform), 3,5-DNPH, mp 152.5-153.5°C (hexane–chloroform) giving no depression of the melting point with an authentic sample; and dehydroabietinal, mp 84-85°C (hexane), $[\alpha]_D^{22}+64°$ (c 1.5; chloroform) (literature data [5]: mp 86-87°C, $[\alpha]_D^{20}+66.5°$). The IR and NMR spectra of all the aldehydes isolated corresponded to those for authentic samples.

In addition to the compounds mentioned, one previously undescribed aldehyde was isolated which made up about 50% of the carbonyl fraction and was identified as abieta-8(9),13(14)-dien-18-al (palustral) (I), mp 54.5-55.5°C (ethanol), $[\alpha]^{20}+59°$ (c 4.24; chloroform), $\lambda_{max}^{C_2H_5OH}$ 564 nm (log ε 3.84). The identification of this aldehyde as palustral was confirmed by its NMR spectrum and its conversion into abietinal under the action of HCl in hexane. Palustral has not been isolated previously from plant sources, although indirect evidence has been obtained of its presence in two species of Pinus [6, 7].

The corresponding alcohol, palustrol (abieta-8(9),13(14)-dien-18-ol) (II) with $[\alpha]_D^{23}+53°$ (c 2.64: chloroform), p-nitrobenzoate, mp 131-132°C (CCl_4–ethanol), $\lambda_{max}^{heptane}$ 267 nm (log ε 3.87), $\nu_{max}^{CCl_4}$ 1060, 3640 cm^{-1} (primary OH) we isolated from the fraction of monohydrate alcohols by chromatographing it on SiO_2 + 5% $AgNO_3$. The formation of abietinol on isomerization with hydrogen chloride in hexane and the characteristics of the NMR spectrum [CCl_4, internal standard HMDS; 0.73 and 1.00 ppm, singlets, 3H each, C_4-CH_3, $C_{10}-CH_3$; 0.95 ppm, 6H, doublet, J = 6.5 Hz, $-CH(CH_3)_2$; 3.16 ppm, 2H, AB system with J_{AB} = 10.5 Hz, and centers of doublets at 2.99 and 3.34 ppm, C_4-CH_2OH; 5.25 ppm, 1H, broad singlet, H_{14}] permitted this previously undescribed diterpenoid to be identified.



I R = CHO
II R = CH_2OH

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From the mixtures of alcohols in addition to palustrol we obtained isopimarinol with mp 85-86°C (hexane), $[\alpha]_D^{20} - 23.1°$ (c 1.90; chloroform) (literature data [3]: mp 85-86°C, $[\alpha]_D - 24.6°$).

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