FORMATION OF NORDITERPENOIDS IN THE AUTOOXIDATION OF DITERPENE ALDEHYDES

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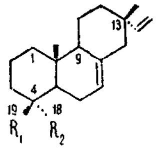
We have previously reported the isolation from the oleoresin of conifers of norditerpenoids with dehydroabietane, isopimarane and pimarane carbon skeletons [1-3]. Similar compounds have been obtained by other authors [4-6]. The origin of the $C_{18}-C_{19}$ norditerpenoids has so far remained obscure.

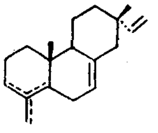
In order to study this question, we left isopimara-7,15-dien-18-al in the air at room temperature for three days. Chromatographic separation of the autooxidation products yielded isopimaric acid (4%), the initial aldehyde (45%), and two comparatively unstable hydroperoxides [(Ia) (8%) and (Ib) (16%); when chromatographed on air-dry SiO_2 they were partially reduced to the corresponding alcohols], which were characterized in the form of their acetates (Ic) [mp 86-87°C (from ethanol), $[\alpha]^{23}_{D}-48.6°$ (c 2.47; chloroform)] and (Id) [mp 58-59°C (from ethanol), $[\alpha]^{20}_{D}-35.6°$ (c 4.49; chloroform)] having the characteristic absorption band of a peroxyacetate carbonyl ($\nu^{CCl_4}_{max}$ 1785 cm^{-1} [7]). When (Ia) and (Ib) were reduced with lithium tetrahydroaluminate in diethyl ether, the corresponding alcohols were formed: (Ie) [mp 50-51°C (from petroleum ether), $[\alpha]^{20}_{D}-38.5°$ (c 0.46; chloroform), M^+ 274] and (If) [mp 124°C (from petroleum ether), $[\alpha]^{20}_{D}-36.5°$ (c 0.29; chloroform)]; literature data: mp 117-118°C, $[\alpha]_D-38°$ [4].

Among the autooxidation products was also found a mixture of hydrocarbons (2%) containing about 5% of a mixture of isopimaratrienes (II) and 95% of a diene (III), $[\alpha]^{22}_{D}-45.6°$ (c 3.53; chloroform); n^{20}_{D} 1.5115; M^+ 258. A sample of (III) that was pure according to TLC consisted according to GLC (E-301) of two components (5 : 1) with retention times of 30 and 36 min, respectively. The formation of (III) is an interesting fact showing the occurrence of a decarbonylation of isopimarinal induced by molecular oxygen. We have not investigated the products of the further oxidation of isopimarinal, amounting to 25%.

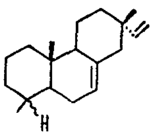
Similar results were obtained in the autooxidation of dehydroabietinal and of epitorulosal. The ease of autooxidation of the aldehydes and the instability of the intermediate hydroperoxides give grounds for assuming that one of the possible routes for the formation of 4-hydroxy-18-nor- and 4-hydroxy-19-norditerpenoids is the autooxidation of the corresponding aldehydes.



I



II



III

	a	b	c	d	e	f
R_1	OOH	Me	OOAc	Me	OH	Me
R_2	Me	OOH	Me	OOAc	Me	OH

Two 4-hydroxy-18-norditerpenoids have been detected in small amount in the oleoresin of Pinus sibirica R. Mayr and identified: 18-norabieta-8,11,13-trien-4α-ol with mp 92-94°C (from petroleum ether) $[\alpha]^{20}_{D}+59.5°$ (c 0.29; methanol) {literature data: mp 89-91°C, $[\alpha]^{20}_{D}+45°$ (c 2.0; chloroform) [5]} and (If) with mp 115-117°C (from petroleum ether), giving no depression with an authentic sample.

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