# STRUCTURES OF LAPIDOLIN AND LAPIDOLININ

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Plants of the genus *Ferula* from different growth sites differ by the quantitative variety of their esters. Esters of the camphane and germacrane types have been detected previously in *Ferula lapidosa* Eug. Korov. from the Buam gorge and the Susamyr valley, KirgSSR [1, 2]. In a study of an extract of the roots of *F. lapidosa* collected in the Chigirik Pass, KirgSSR, we have isolated five carotane esters. We give information on the determination of the structures of two of them — lapidolin and lapidolinin.

Lapidolin (I), $C_{24}H_{36}O_8$, $M^+$ 452, mp 188–189°C (ethanol), $[\alpha]_D^{20}$ +27.7° (c 1.3; chloroform). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 218 nm (log ε 3.72). IR spectra cm$^{-1}$: $\nu_{max}^{KBr}$ 1755 (C=O of an ester), 1720 (C=C–C=O of an ester), 1240 ester–C–O bands), 970, 1650 (>C=CH), 3500 (OH).

The PMR spectrum ($CDCl_3$, δ scale, 0 — HMDS) shows the signals of the protons of an isopropyl grouping — doublets at 0.83 and 0.85 ppm (3 H each, J = 7 Hz); of an angular methyl group — 1.25 ppm (s); and of a methyl attached to a carbon atom bearing an oxygen function — 1.41 ppm (s). In addition, there are the signals of an epoxide proton — 2.8 ppm (d, J = 5 Hz) — and of three gem-acyl protons — 4.87 ppm (d, J = 6 Hz), 5.2 ppm (d, J = 5 Hz), and 5.32 ppm (m, $\Sigma_{1/2}$ = 24 Hz), and also the signals of the protons of two acetyl residues and an angeloyl residue.

The presence of these functional groups in the molecule of (I) was confirmed by its mass spectrum, which contained the peaks of ions with m/z 409$(M - C_3H_7)^+$, 349$(409 - CH_3COOH)^+$, 309$(409 - C_5H_8O_2)^+$, 249$(349 - C_5H_8O_2)^+$, 266$(309 - CH_3CO)^+$, 232$(249 - 17)^+$.

Lapidolinin (II), $C_{28}H_{38}O_{10}$, $M^+$ 534, mp 182-183°C (ethanol), $[\alpha]_D^{20}$ +54.5° (c 1.1; chloroform). UV spectrum, nm, $\lambda_{max}^{C_2H_5OH}$: 211, 264, 295 (log ε 4.32, 4.8, 3.83). IR spectrum, cm$^{-1}$: $\nu_{max}^{KBr}$ 1760, 1710, 1230–1280 (ester C=O and –C–O groups), 1520, 1600 (aromatic nucleus), 3550 (OH).

The PMR spectrum (II) basically repeats that of lapidolin, but differs from the latter in containing the signals of the protons of a veratric acid residue in place of an angelic acid residue [q, 7.60 ppm (1 H, J = 9 and 2.5 Hz); d, 6.78 ppm (1 H, J = 9 Hz); d, 7.36 ppm (1 H, J = 2.5 Hz); s, 3.85 and 3.88 ppm (3 H each)].

The presence of a veratroyl residue in the molecule of (II) was confirmed by the corresponding ion peaks in the mass spectrum, with m/z 352 $(M - C_9H_{10}O_4)^+$ and 309 $(491 - C_9H_{10}O_4)^+$.

A comparison of the facts given with information in the literature [3–8] showed that both substances belonged to the carotane derivatives (as was confirmed by the formation of daucalene when they were dehydrogenated with Pd.

The alkaline hydrolysis of (I) and (II) formed angelic and veratric acids, respectively, and the same carotane alcohol lapidolinol, $C_{15}H_{26}O_5$, mp 260–261°C (decomp.), $[\alpha]_D^{20}$ +58° (c 1.1; ethanol).

A comparative analysis of the PMR spectra of lapidolinol and of isolaserol [6] showed that they differed practically solely by the multiplicity of the signal of one hemihydroxylic

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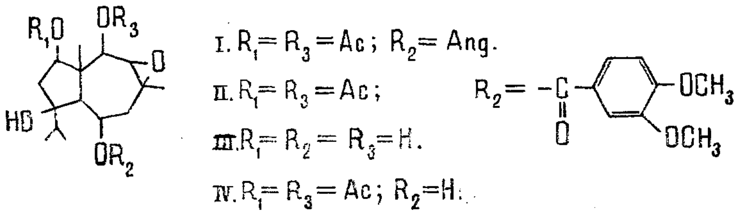
proton, which in the first case was a doublet with broadened components at 4.01 ppm, J = 5 Hz, and in the second case was a quartet at 3.73 ppm with J = 11.5 and 8 Hz. This is due to the different orientations of the protons at $C_2$, and consequently of the hydroxyl groups geminal to them in the compounds being compared. Hence, the structure of lapidolinol is expressed by structural formula (III).


I. $R_1 = R_3 = Ac$; $R_2 = Ang$.
II. $R_1 = R_3 = Ac$; $R_2 = -C(=O)-C_6H_3(OCH_3)_2$
III. $R_1 = R_2 = R_3 = H$.
IV. $R_1 = R_3 = Ac$; $R_2 = H$.

The mild hydrolysis of (I) and (II) (with $Na_2CO_3$ solution) also gave angelic and veratric acids, respectively, and the same diacetate (IV), $C_{19}H_{20}O_7$, mp 210–211°C. The PMR spectra of the latter retained the signals of both acetyl residues, while the multiplet relating to the proton at $C_6$ had shifted upfield to 4.6 ppm. It follows from this that the angelic acid in (I) and the veratric acid in (II) esterified the hydroxy groups at $C_6$, and in both compounds the acetyl residues were located at $C_2$ and $C_{10}$. Thus, lapidolin and lapidolinin have the structures I and II, respectively.

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