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ISOCUPRESSIC ACID AND NEW ESTERS OF IT FROM THE NEEDLES OF *Pinus sibirica*

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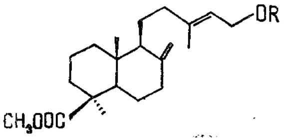
In view of the potential significance of diterpene acids from needles in the chemosystematics of coniferous plants [1], we have investigated the "polar" resin acids [2] of the needles of *Pinus sibirica* R. Mayr. (Siberian stone pine).

It has been shown previously [3] that the ordinary resin acids of these needles are represented by lambertianic acid and tricyclic acids of the abietane and isopimarane series.

The acid fraction of an ethereal extract of the air-dry needles collected in March, 1983, was methylated with diazomethane and chromatographed on silica gel as described previously [2]. In this way, three compounds were obtained, with yields of 4, 1, and 0.2% on the initial acid fraction. The main compound was identified from its PMR spectrum and its constants as methyl cupressate (I), which has been found previously in the oleoresin of the Siberian stone pine [4]. The other two proved to be new substances, not previously described, and their structures have been established as the dimethyl ester of 15-O-succinylisocupressic acid (II) and methyl 15-O-methylisocupressate (III).



I. R = H
II. R = CH_3
III. R = $COCH_2CH_2COOCH_3$

In the PMR spectrum (here and below, 60 MHz, CCl_4, HMDS, δ scale) of substance (II), which was obtained in the form of an oil with n_D^{27} 1.5000, $[\alpha]_D^{27}$ +34.8° (c 8.93; chloroform), the characteristic singlet [2] of the four protons of the methylene groups of a succinyl residue was observed at 2.47 ppm, the singlets of two methoxycarbonyl groups at 3.53 and 3.59 ppm, and a doublet (J = 7 Hz, 2H) of the protons of the C_{15}-methylene group at 4.53 ppm. In addition, there were signals at (ppm) 0.43, 1.10, and 1.63 (3H each, singlets, Me_{10}, Me_4, and Me_{13}, respectively), 4.47 and 4.80 (1H each, narrow multiplets, $>C{=}CH_2$), and 5.25 ppm (1H, triplet, J = 7 Hz, H_{14}). When the ester (II) was reduced with lithium tetrahydroaluminate in diethyl ether, the known [4] agathadiol with mp 108-109°C was obtained.

The ester (III) (yield 0.2%) was obtained in the form of an oil with n_D^{20} 1.5070, $[\alpha]_D^{20}$ +38° (c 1.45; chloroform). PMR spectrum (ppm): 5.23 (1H, triplet, J = 7 Hz), 3.80 (2H, doublet, J = 7 Hz) and 3.16 (3H, singlet) — the protons of a $>C{=}CH{-}CH_2{-}OCH_3$ grouping, 4.81 and 4.48 (1H each, narrow multiplets, $>C{=}CH_2$), 3.53 (3H, singlet, $COOCH_3$), 1.58, 1.10, and 0.43 (3H each, singlets, Me_{13}, Me_4, and Me_{10}, respectively). The structure of this ester was shown by its formation in the methylation of methyl isocupressate (I) with methyl iodide in tetrahydrofuran in the presence of sodium hydroxide.

15-O-Succinylisocupressic acid is present in the needles in the form of a free diacid, and not the monomethyl ether since, like agathic acid [2], it is selectively extracted by an aqueous solution of sodium bicarbonate from ethereal solutions both of the acid fraction and of the whole extract of the needles. 15-O-Methylisocupressic acid is not the product of

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the reaction of diazomethane with isocupressic acid, since under the conditions of methylation the alcohol group of the latter is not affected (checked in a model experiment).

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