

CHEMISTRY OF *Pinus sylvestris* CONES

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The chemical composition of the individual organs (needles, needleless runners, buds, cones) of common pine (*Pinus sylvestris* L.) was studied in order to develop and improve industrial reprocessing of green wood. Second-year cones have not been studied previously. We attempted to find the dominant components of the extract.

Raw material (195 g calc. for absolute dry material) was collected on the banks of Lake Baikal in Bol'shie Koty village during July 2003 and was preserved in ethanol at the collection site in order to prevent fermentation. The concentrated ethanol extract (54 g) was extracted exhaustively with CHCl_3 and then butanol. The CHCl_3 extract (10 g) was repeatedly chromatographed over silica gel to isolate dehydroabietic acid (**1**, 60 mg) and a sterol fraction (15 mg). The butanol extract (21 g) afforded (-)-catechin (**2**, 100 mg), shikimic acid (**3**, 700 mg), and β -sitosterol glucoside (**4**, 54 mg). The pure compounds were identified by spectral methods including 2D NMR. Signals for C atoms were assigned to the corresponding signals for H atoms using ^1H — ^{13}C HETCOR. Through-space C—H pairings were found using ^1H — ^{13}C HMBC.

Free sterols comprised β -sitosterol (M^+ 414), stigmasterol (M^+ 412), and campesterol (M^+ 400) according to GC—MS (Agilent HP 6890-5973 N).

Dehydroabietinic acid (1): amorphous powder, $[\alpha]_{546}^{23} +74^\circ$ (c 1.2, CHCl_3) [1]. The ^{13}C NMR spectrum was identical to that in the literature [2].

(-)-Catechin (2): mp $184\text{--}186^\circ\text{C}$, $[\alpha]_{546}^{23} -10^\circ$ (c 0.8, CH_3OH) [3]. The ^{13}C NMR spectrum agreed the that in the literature for 2,3-*trans*-isomers of flavan-3-ols [4]: chemical shifts were 81.41 ppm for C-2 and 67.38 ppm for C-3. The spin—spin coupling constants for H-2 and H-3 were 7.5 Hz, which confirmed the *trans*-position of the substituents on C-2 and C-3 [5]. The negative rotation angle of the plane of polarized light for **2** enabled one of the two optical isomers of catechin to be selected.

Shikimic acid (3): mp 184°C (ethanol), $[\alpha]_{546}^{24} -206^\circ$ (c 2.1, ethanol) [1].

β -Sitosterol glucopyranoside (4): mp $267\text{--}270^\circ\text{C}$ (CH_3OH), $[\alpha]_{546}^{25} -38^\circ$ (c 0.9, pyridine) [6]. Compound **4** was identified by comparing its physical chemical constants with those in the literature and by its chromatographic behavior. All compounds were isolated from common pine cones for the first time.

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