ACETOPHENONE GLYCOSIDES FROM THE NEEDLES OF *Picea obovata*

S. Z. Ivanova, S. A. Medvedeva
V. K. Voronov, and N. A. Tyukavkina

UDC 153.21.67

From the butanol fraction [1] of a methanolic extract of the needles of *Picea obovata* Ledeb. (Siberian spruce) collected in August, 1973, by chromatography on polyamide and silica gel impregnated with sodium metabisulfite (2%) with elution by chloroform containing increasing proportions of methanol, we have isolated three compounds:

(I) − p-hydroxyacetophenone glucoside, mp 183-185°C, $[\alpha]_D^{22} - 55.0°$ (c 1.0; pyridine), λ_{max} (CH_3OH) 265 nm (log ε 3.97); (II) − 3,4-dihydroxyacetophenone 3-glycoside, mp 200-202°C, $[\alpha]_D^{22} - 65.0°$ (c 1.0; pyridine), λ_{max} (CH_3OH) 272 nm (log ε 4.09); and (III) − 4-hydroxy-3-methoxyacetophenone glucoside, mp 206-208°C, $[\alpha]_D^{22}$ $- 86.03°$ (c 0.84; pyridine), λ_{max} 268, 300 nm (log ε 3.95, 3.8).

The PMR spectra of the TMS ethers of these compounds each showed a singlet at δ 2.45 cm (3H) of a CH_3 group. The aromatic protons H-3, H-5 and H-2, H-6 of compound (I) appeared in the form of doublets at δ 6.93 ppm (2H) and 7.83 ppm (2H), with J = 8 Hz. The signal of the H-5 proton in compounds (II) and (III) appeared at δ 6.77 ppm (1H) in the form of a doublet with $J_{5,6} = 8$ Hz, and the H-6 and H-2 protons gave an unsymmetrical doublet with its center at δ 7.41 ppm (2H), $J_{6,5} = 8$ Hz. The protons of the methoxy group in compound (III) appeared in the form of a singlet at δ 3.71 ppm (3H).

The PMR spectra were taken on a BS 487B spectrometer in CCl_4 as solvent with HMDS as internal standard.

The aglycones obtained by the acid hydrolysis of the glycosides were identified by GLC in the form of their PMS ethers on the basis of the results of a comparison with authentic samples of p-hydroxyacetophenone (RT 5.25 min, taken as 1.0), 4-hydroxy-3-methoxyacetophenone (RRT 1.84), and 3,4-dihydroxyacetophenone (RRT 2.38).

GLC analysis was performed on a "Tsvet-4" instrument with a flame-ionization detector; column 300 × 0.3 cm filled with 5% of SE-30 on Chromaton N-AW-HMDS with helium as the carrier gas. The column temperature was 176°C.

Glucose was identified in hydrolyzates neutralized on AV-17 ion-exchange resin. According to their PMR spectra, the compounds isolated were monosides. Positive hydrolysis with the enzyme of *Aspergillus oridasa* and the presence of doublets at δ 4.87 ppm (J = 6 Hz) in the PMR spectrum of compounds (I) and (III) and at δ 5.37 ppm (J = 6 Hz) for (II) showed the β-D-pyranose form of the glucose substituent.

We also isolated 3,4-dihydroxyacetophenone in the free form by preliminary extraction with diethyl ether of a methanolic extract of the needles of *Picea obovata* and identified it from its physicochemical constants: mp 116-117°C, λ_{max} (CH_3OH) 275, 305 nm (log ε 3.78, 3.63); mol. wt. 152 (mass spectrometry), and the characteristics of its PMR spectrum.

3,4-Dihydroxyacetophenone and its glucoside, and also p-hydroxyacetophenone glucoside, have been found previously in the needles of some other species of spruce [2-6]. This is the first time that 4-hydroxy-3-methoxyacetophenone glucoside has been found in the needles of the genus *Picea*.

LITERATURE CITED

1. S. Z. Ivanova, S. A. Medvedeva, N. A. Tyukavkina, and N. D. Zelenikina, Khim. Prirodn. Soedin., 415

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 107-108, January-February, 1976. Original article submitted August 20, 1975.

(1975).
2. M. Tanret, Bull. Soc. Chim. Fr., 11, 944 (1894).
3. A.C. Neish, Canad. J. Biochem. Physiol., 35, 161 (1957).
4. A. C. Neish, Canad. J. Botany, 36, 649 (1958).
5. M. Takahashi, T. Ito, and A. Mizutani, J. Pharm. Soc. Japan, 80, 782 (1960).
6. M. Takahashi, J. Pharm. Soc. Japan, 81, 934 (1961).

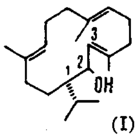
CONFIGURATION OF THE DOUBLE BOND AND PARTIAL SYNTHESIS OF ALLYLCEMBROL

V. A. Raldugin, O. B. Shelepina,
I. P. Sekatsis, A. I. Rezvukhin,
and V. A. Pentegova

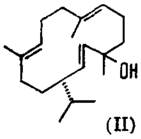
UDC 547.595.9+547.366+547.385

From the epigeal part of Commiphora mukul, Ruker [1] isolated a new cembrane alcohol, which he called allylcembrol. This compound has been isolated by Patil [2] from the resin of the same plant under the name of "mukulol." The structure of allylcembrol (I) was shown by the production of cembrene from it on mild dehydration and on the basis of spectral characteristics. The configurations of the C_3 double bond and of the C_2 asymmetric center remained unknown. We have synthesized allylcembrol and its C_2 epimer from isocembrol (II).

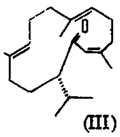
The treatment of isocembrol with the Jones reagent in aqueous acetone (0°C, 30 min) gave a complex mixture the chromatography of which on SiO_2 (petroleum ether containing increasing concentrations of diethyl ether as eluent) gave successively fractions of hydrocarbons (yield 24%), ketones (20%), epoxyketones (21% – mixture of three stereoisomeric 3,4-epoxycembra-7,11-dien-2-ones), and 2,3-epoxycembra-7,11-dien-4-ol (30%) with mp 94-95°C (from ethanol), $[\alpha]_D^{20}$ +44.4° (c 5.43; chloroform). The ketone fraction was rechromatographed on SiO_2. The first ketone isolated from the column was (III) with n_D^{22} 1.5166, $[\alpha]_D^{22}$ +110.1° (c 5.43; chloroform); IR spectrum (in CCl_4) 1690, 1625, 1385 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 242 nm (log ε 3.97); NMR spectrum (here and below, in CCl_4, 100 MHz, TMS, ppm): 1.53 (6H, C_8-CH_3 and $C_{12}-CH_3$), 1.81 (3H, C_4-CH_3), 4.6-5.1 (2H, multiplet, H_7 and H_{11}), and 5.95 (1H, narrow multiplet, H_3).



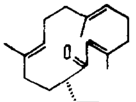
(I)



(II)



(III)



(IV)

The second ketone (IV) with n_D^{22} 1.5040, $[\alpha]_D^{23}$ +106.9° (c 8.84; chloroform) was identical, according to its NMR spectrum, with a ketone isolated by Patil from mukulol. The absence of an intramolecular nuclear Overhauser effect between H_3 and C_4-CH_3 in the ketone (IV) shows [3, 4] the trans configuration of the C_3 double bond and, consequently, the trans configuration of the same bond in allylcembrol (mukulol). Thus, the second ketone has a cis configuration of the C_3 double bond. This could not be shown by means of the Overhauser effect, since when the oxygen was eliminated by Kaiser's method [5] from a solution of the ketone (III) in CCl_4 it isomerized completely into the trans ketone (IV). A mixture of equal amounts of these ketones was obtained after a 5% solution of the ketone in CCl_4 had been kept at 20°C for a week. A similar instability of a macrocyclic cis-2-enone system has also been observed by Nozaki [6] for cis-dodecen-2-one.

The reduction of the ketone (IV) with $LiAlH_4$ in diethyl ether (20°C, 5 min) gave a mixture of secondary alcohols which was chromatographed on SiO_2 + 5% $AgNO_3$. Petroleum ether containing 10% of diethyl ether

---

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 108-109, January-February, 1976. Original article submitted June 14, 1975.