TRITERPENOIDS FROM Abies SPECIES.
I. ABIESONIC ACID — A TRITERPENOID WITH A NEW
CARBON SKELETON FROM THE OLEORESIN OF Abies sibirica

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The structure and stereochemistry of abiesonic acid — a new triterpenoid with a
modified 3,4-secolanostane carbon skeleton isolated in the form of the dimethyl
ester from the oleoresin of the Siberian fir — has been established with the aid
of x-ray structural analysis. On irradiation with UV light, this ester is con-
verted reversibly into its 24Z- isomer.

A feature of the chemical composition of the needles and bark of some species of fir is
the presence of highly polar neutral triterpenoids of the 9β-lanostane [1-4] or cycloartane
[5, 6] series, the first of which to be described was abies lactone (I) [1, 2]. In the
seeds of the fir Abies mariesii, Hasegawa has found a whole series of triterpene acids,
for one of which (mariesiic A) he established structure II with a rearranged lanostane carbon
skeleton.

We have shown previously [8] that a substantial part of the acid fraction of the oleo-
resin of the Siberian fir is composed of triterpene acids, two of which were isolated in the
form of methyl esters and were characterized by their constants and some spectral properties.
In the present communication we give the results of the determination of the structure of one
of them — abiesonic acid, obtained in the form of the dimethyl ester from a mixture of the
dimethyl esters of the "strong acid" fraction [8] of the oleoresin by chromatography on
silica gel.

Dimethyl abiesonate crystallizes well from acetonitrile or pentane. The structure and
relative configuration of its molecule were established by x-ray structural analysis and are
expressed by formula (3) and shown in Fig. 1. The six-membered ring has the usual half-
Fig. 1. Structure and relative configuration of the dimethyl abiesonate molecule (III). The probable errors in the bond lengths are 0.01-0.02 Å.

chair form and both five-membered rings have the envelope form, deviations of the C₁₁ and C₁₇ atoms from the planes formed by the other atoms of these rings being 0.62 and 0.64 Å, respectively. The carbon atoms and one oxygen atom of the C₁₃-O-Cₑ₈=c=O-C₂₂ (-C₂₇)=C₂₄ fragment in one plane, while the carbonyl group at C₂₃ departs from it. The C₂₂=C₂₄-C₂₃=c=O torsional angle is 27°. The side chain at C₁₀ is also practically planar.

Formula (III) also, apparently, expresses the absolute configuration of the dimethyl abiesonate molecule (Fig. 1 shows its enantiomeric structure), since the configuration at C₁₀ and C₅ in it are the "natural" ones and correspond to the absolute configuration at these centers in the molecules of all known natural (not rearranged in the area of rings A and B) triterpenoids.

The UV spectrum of the compound under investigation has a maximum at 238 nm (log ε 2.54, in ethanol) corresponding to an electronic transition in an α-enone system. The corresponding Cotton effect on the circular dichromism curve has a negative sign.

In the PMR spectrum, the protons of the exomethylene groups give signals at 4.70 ppm (1 H, H₂₅, 4.79 ppm (2 H, H²₁₀ and H²₁₈), and 4.81 ppm (1 H, H²₁₆) in the form of narrow multiplets. Their assignment was confirmed by double resonance with the suppression of the signal of the C₄-methyl group appearing at 1.72 ppm. The Jₐₕ value for the C₂₆ protons was 2.5 Hz. The signal of the H₂₄ proton is a quartet at 7.00 ppm (J = 1.2 Hz) and that of the protons of the C₂₅-methyl group protons a double at 2.17 ppm with the same spin-spin coupling constant (1.2 Hz). The signal of the protons of the C₂₆-methoxycarbonyl group is shifted downfield from its usual position for them because of the electron-accepting influence of the C₂₃-keto group and appears at 3.79 ppm (singlet). The signal of the protons of the second methoxycarbonyl group appears in the form of a similar singlet at 3.64 ppm. The H₂ proton gives a signal at 5.46 ppm in the form of a quartet (J ~ 3 Hz) with poorly resolved lateral components. The angular methyl groups appear in the form of singlets at 0.87 and 0.89 ppm and the secondary methyl group (Me₂₂) in the form of a doublet (J = 6.0 Hz) at 0.81 ppm. The ¹³C NMR spectrum (see the Experimental part) agrees with structure (III).