Lanostane Lactols from the Needles of Siberian Fir

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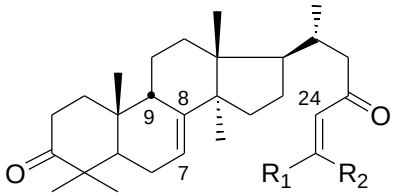
Needles of Siberian fir (*Abies sibirica* Ledb.) are a rich source of triterpenoids of the 9?-lanostane series most of which are carboxylic acids.



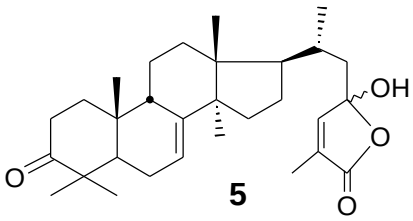
1 - 4

1: $R_1 = COOH$; $R_2 = CH_3$

2: $R_1 = CH_3$; $R_2 = COOH$

3: $R_1 = CH_3$; $R_2 = COOCH_3$

4: $R_1 = COOCH_3$; $R_2 = CH_3$



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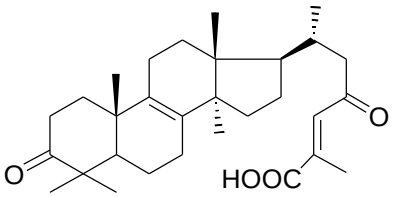

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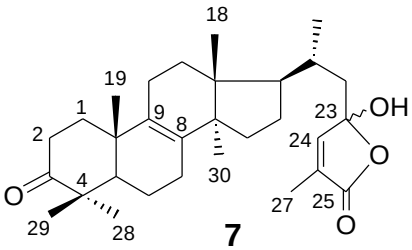

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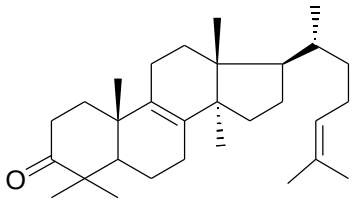

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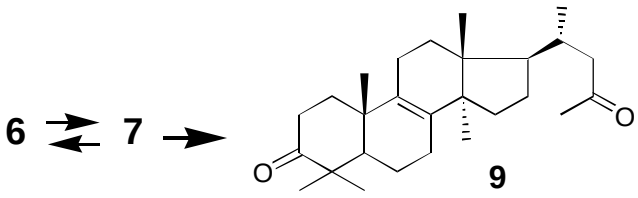
Isomeric acids **1** and **2** are the first compounds of this type reported in the literature. Acid **2** ((24Z)-isomer) was characterized only as its methyl ester **3**. Acid **2** is, apparently, prone to undergo conversion into the cyclic tautomer **5**. More recently, compound **5** was isolated from a mixture of free acids extracted from fir needles.

Methyl ester of acid **6** was identified as the minor component of the methylated mixture of acids from the fir needles. Not long ago we found the (24Z)-isomer of this acid, which also exists as the cyclic lactol **7**. The NMR ^1H spectrum of **7** may be considered as a superposition of the spectrum of the known **8** and the spectrum of the lactone fragment of **5**. Formula **7** describes also the absolute configuration of this molecule (determined by CD). Both lactols **5** and **7** are crystalline non-separable mixtures of 23-epimers (NMR ^{13}C and ^1H).



9

Controlled heating of **7** (NaOH/EtOH/70° C) leads to crystalline diketone **9** as a result of fragmentation. This process was readily monitored by HPLC on reversed phase column with double-wavelength photometric detection (200 and 240 nm). Acid **6** was formed initially, and then compounds **6** and **7** were gradually converted into diketone **9.** Substances **4** and **5** behave in a similar manner. The (24Z)-isomers of acids **1** and **6** were detected by HPLC as tautomers **5** and **7** because of the acidic nature of the eluent ($MeOH/H_2O/H_3PO_4$).