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STRUCTURE OF TRIPHYLLIC ACID

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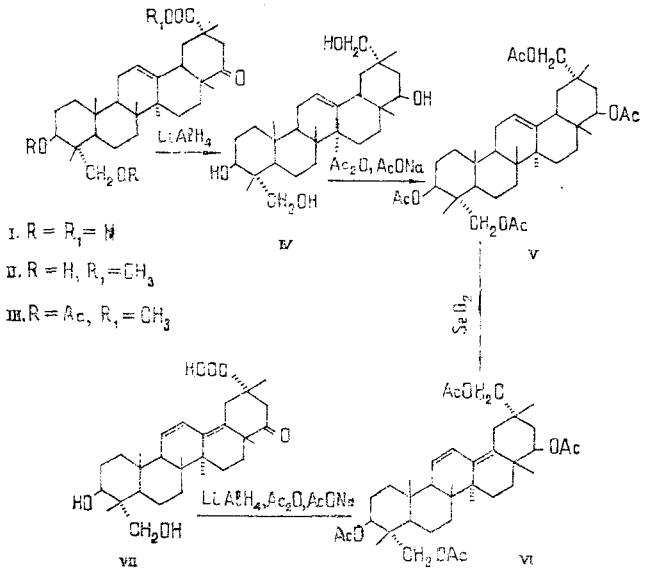
On the basis of chemical transformations and spectral characteristics, the structure of a pentacyclic triterpenoid isolated from the roots of *Glycyrrhiza triphylla* Fisch. et Mey, triphyllic acid, has been established as 3β,24-dihydroxy-22-oxoolean-12-en-29-oic acid.

The structures of pentacyclic triterpenoids of *Glycyrrhiza triphylla* Fisch. et Mey, family Fabaceae — meristotropic acid [1, 2], isomeristotropic acid [3], and hydroxymeristotropic acid (VII) [4] — and also the isolation of triphyllic acid (I) [5] have been reported previously. The last-mentioned compound also belongs to the β-amirin series. In the present paper we give a proof of the structure of triphyllic acid (I).

The substance under consideration (I) is a dihydroxyoxotriterpene acid [5]. According to its elementary composition, $C_{30}H_{46}O_5$, triphyllic acid contains one double bond, as was confirmed by a positive reaction with tetranitromethane.

Reduction of methyl triphyllate (II) with lithium tetrahydroaluminate gave compound (IV) the IR spectrum of which lacked the absorption due to a carbonyl group. Consequently, product (IV) must have been a tetraol. In actual fact, the acetylation of substance (IV) led to the formation of a tetraacetate (V) (M^+ 640). In the mass spectrum of compound (V), the peaks of ions with m/z 334 and 307, formed as the result of a retrodiene breakdown [6], unambiguously determined the position of the double bond at C-12.



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In the PMR spectrum of the diacetate of methyl triphyllate (III) described previously [5] a one-proton multiplet of the olefinic proton at C-12 appeared at 5.25 ppm [7]. This fact is evidence in favor of the conclusion that the double bond is located at C-12. In the same PMR spectrum a triplet with Σ^3J = 15 Hz appeared at 4.53 ppm and a two-proton quartet of the type of system $^2J_1 = {}^2J_2$ = 12 Hz at 4.25 ppm, which have been assigned, respectively, to 3α-H and to the two methylene protons of an acetoxymethyl group having the axial orientation [1-10]. Consequently, the secondary hydroxyl group of triphyllic acid is located at C-3 and has the β orientation, the primary hydroxy group being at C-24. The CD spectrum of methyl triphyllate (II) showed a positive Cotton effect at 296 nm ($\Delta\varepsilon$ = +3.28), like methyl meristotropate and hydroxymeristotropate [4].

This permitted us to suggest that in triphyllic acid ketonic carbonyl group is located at C-22.

The acetylation of triphyllic acid took place like those of meristotropic and hydroxymeristotropic acids, giving acetates of mixed acid anhydrides [11], which confirmed the position of the carboxy group at C-29.

For a definitive determination of the positions of all the functional groups we performed a correlation of triphyllic acid (I) with hydroxymeristotropic acid (VII). For this purpose, the oxidation of the tetraacetate (V) with selenium dioxide yielded a product (VI) identical with the tetraacetate of hydroxymeristotropic acid [4].

These results show the identity of the positions of all the oxygen functions in the two triterpenoids (I) and (VII). Consequently, unlike hydroxymeristotropic acid (VII), which is a conjugated diterpene, triphyllic acid (I) has a single double bond at C-12.

For triphyllic acid (I) we propose the structure of 3β,24-dihydroxy-22-oxoolean-12-en-29-oic acid.

EXPERIMENTAL

For thin-layer and column chromatography we used alumina (inactive). IR spectra were taken on a UR-20 spectrophotometer in paraffin oil, PMR spectra on a Varian HA-100 spectrometer in deuterochloroform (δ, ppm, 0 — HMDS), and mass spectra on a MKh-1310 instrument. For the isolation of triphyllic acid (I) and the preparation of the methyl ester (II) and the diacetate of the methyl ester (III), see [5]. CD of the methyl ester (II): $\Delta\varepsilon$ = +2.90 (λ 296 nm; c, 3 mg in 4 ml; ethanol).

PMR spectrum of the diacetate of the methyl ester (III): 0.88 (3 H, s, CH_3); 1.02 (3 H, s, CH_3); 1.05 (6 H, s, 2 × CH_3); 1.19 (3 H, s, CH_3); 1.22 (3 H, s, CH_3); 2.02 (6 H, s, 2 × CH_3COO); 3.66 (3 H, s, CH_3O); 4.25 (2 H at C-24, q, $^2J_1 = {}^2J_2$ = 12 Hz); 4.53 (1H at C-3, m, Σ^3J = 15 Hz); 5.25 (1 H at C-12, m).

The Tetraol (IV) from (II). A solution of 0.5 g of methyl triphyllate (II) in 15 ml of absolute tetrahydrofuran was treated with 0.25 g of lithium tetrahydroaluminate and the mixture was heated on the water bath for 7 h. Then 25 ml of ethyl acetate, a solution of sodium sulfate, and water was gradually added until the mixture separated into layers. The reaction product was extracted with ether. After the solvent had been distilled off, recrystallization of the residue from ethanol yielded (IV), $C_{30}H_{50}O_4$, mp 309-313°C. The IR spectrum of the tetraol (IV) lacked the absorption due to a carbonyl group.

The Tetraacetate (V) from (IV). A mixture of 0.2 g of the tetraol (IV), 15 ml of acetic anhydride, and 0.15 g of sodium acetate was heated for 7 h. Then 15 ml of water was added to the reaction mixture and it was heated for another 15 min. After this, 50 ml of water was added and the resulting precipitate was filtered off. Recrystallization from ethanol gave the tetraacetate (V), $C_{38}H_{58}O_8$, mp 194-196°C. IR spectrum, ν_{max}^{NaCl}, cm^{-1}: 1735, 1250 (ester groups). Mass spectrum, m/z, %: M^+ 640 (3.9), 582 (16.6), 569 (2.9), 522 (3.9), 509 (3.9), 334 (12.7), 307 (2.9), 274 (100), 262 (4.4), 248 (4.9), 232 (7.8), 214 (25.4), 201 (25.4), 188 (13.7).

The Tetraacetate (VI) from (V). A solution of 0.1 g of the tetraacetate (V) in 50 ml of acetic acid was treated with 0.3 g of freshly prepared selenium dioxide and the mixture was heated on the water bath for 23 h. At the end of the reaction, the selenium was filtered off, water was added to the reaction mixture, and the resulting precipitate was separated off and dried. The dried residue was dissolved in chloroform and chromatographed on a column of alumina. When chloroform was used as the eluent the tetraacetate (VI), $C_{38}H_{56}O_8$,

was obtained with mp 158-160°C from ethanol, and also identical with a tetraacetate of hydroxymeristotropic acid [4] according to IR and UV spectroscopy.

SUMMARY

A pentacyclic triterpenoid isolated from the roots of the plant *Glycyrrhiza triphylla* Fisch. et Mey — triphyllic acid — has the structure of 3β,24-dihydroxy-22-oxooleano-12-en-29-oic acid.

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GLYCOSYLATION OF BETULIN AND ITS ACETATES IN THE PRESENCE OF CADMIUM CARBONATE

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The glycosylation of betulin and its acetates by α-acetobromoglucose in toluene in the presence of cadmium carbonate is considered. It has been shown that the reaction is accompanied by Wagner—Meerwein rearrangements of the initial alcohols in rings A and E. This leads to the formation — in addition to acetates of betulin glycosides — of derivatives of allobetulin — A-nor-$\Delta^{3(5)}$-allobetulin and A-nor-$\Delta^{3(5)}$-betulin — as was shown by ^{1}H and ^{13}C NMR spectroscopy.

Betulin — one of the representatives of the pentacyclic triterpenoids of the lupane series most promising for practical use — is widely distributed in the vegetable kingdom [1, 2]. The main source of betulin is the bark of various species of the genus *Betula* [1-5]. Esters of betulin and higher fatty acids have found use as various protective coatings [6]. A number of plant extracts, the main components of which are betulin, betulinic acid, and lupeol, exhibit an antitumoral action [7, 8].

The availability and biological activity of betulin place it among valuable natural sources for use both in the native state and in the form of various transformation products.

Our aim was to study the conditions for the glycosylation of betulin (I) and its acetates (II) and (III) by α-acetobromoglucose (α-ABG) in the presence of cadium carbonate in toluene [12]. We have previously synthesized some acetylated betulin glycosides by the orthoester and other methods [9-11]. The glycosylation conditions used by Conrow and Bern-

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