

NEW CYCLOARTANE TERPENOID FROM THE OIL OF SEA BUCKTHORN FRUIT

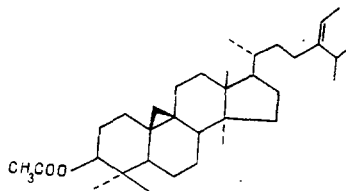
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We have continued the study of the unsaponifiable part of the oil of the fruit of sea buckthorn growing in the Western Pamir [1].

The oil was saponified by a standard method [2]. The unsaponifiable part was separated by column chromatography (CC) on silica gel. After preliminary acetylation, the triterpene fraction was rechromatographed on silica gel that had been treated with silver nitrate (5%) [3], and a narrow fraction of triterpene compounds was isolated which, according to gas chromatography, consisted of 24-methylcycloartane and an unidentified compound. The fraction was separated into its components by preparative liquid chromatography. To determine the structure of the unknown compound we used ^{13}C NMR and PMR spectroscopies and two-dimensional ^{13}C spectroscopy.

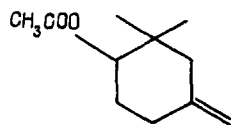
The mass spectrum of the compound isolated was similar to that of 24-methylenecycloartanol acetate, but its M^+ value differed by 14 mass units. On the basis of these facts and also of the indices of the ^{13}C and ^1H NMR spectra we propose the following structure for this compound:



The presence of signals in the weak-field part of the ^{13}C NMR spectrum — at 170.89 ppm — of the carbonyl atom carbon atom of an acetyl group, $-\text{COO}^-$ and of a secondary carbinol carbon atom of a ring linked with an acetate group (CHO) (80.66 ppm) and the absence of other signals of carbons linked with oxygen suggested that the molecule of the compound isolated contained two oxygen atoms. This and also the results of mass spectrometry showed that the elemental composition of the compound was $\text{C}_{34}\text{H}_{56}\text{O}_2$.

A proof of the presence of a cyclopropane ring in the compound was provided by the characteristic signals of a cyclopropane methylene in its PMR spectrum. They appeared in the strong field in the form of two one-proton doublets (an AB system) with the geminal spin-spin coupling constant $^2J = 4$ Hz at 0.34 and 0.58 ppm. These values of the chemical shifts of the protons of the cyclopropane ring showed the presence of two methyl groups at C_4 . If a single methyl group had been present, the chemical shifts would have been 0.11 and 0.36 ppm [4]. This was also shown by the fact that H-3 resonated in the form of a doublet of doublets at 4.75 ppm with the SSCC $^3J_1 = 10.6$ and $^3J_2 = 5.0$ Hz.

The mass-spectrometric fragmentation of the substance under electron impact led to the appearance of an ion with m/z 182. The pathway for the formation of the latter is also characteristic for cycloartanes [4]. Moreover, it can be seen from the PMR spectrum that the proton at C_3 (4.57 ppm) interacted only with the two protons at C_2 , giving a doublet of doublets ($^3J = 10.6$ and 5.0 Hz), i.e., the carbon in position 4 had no unsubstituted protons.



Mass-spectrometric investigations confirmed what has been said above: a signal was detected with m/z 182, corresponding to a structure characteristic for the breakdown of cycloartanes [4]. The chemical shifts of all the carbon atoms of the cyclopropane ring (20.15, 25.98, 26.73 ppm) in the ^{13}C NMR spectrum likewise corresponded to two methyl groups in position 4 [4]. All these facts confirmed the presence of a cycloartane structure in the compound.

By deducting the composition of the polycyclic moiety of the molecule from the elemental composition of the compound ($\text{C}_{34}\text{H}_{56}\text{O}_2$) we found the elemental composition of the side-chain — $\text{C}_{10}\text{H}_{19}$. Analysis of the ^1H and ^{13}C NMR spectra made it possible to establish the structure of the side-chain. Signals in the ^{13}C NMR spectra at 116.5 ppm from a $=\text{CH}$ group and at 145.87 ppm from a quaternary carbon atom at a double bond, and also signals in the PMR spectrum — the quartet (5.13 ppm) of a methine proton interacting with a methyl group (doublet at 1.59 ppm, $^3J = 6.7$ Hz) could be assigned only to a terminal $=\text{CH}^{\text{H}3}$ group.

It was possible to assign signals in the PMR spectrum — a septet at 2.83 ppm and a doublet of methyl groups at 0.98 ppm unambiguously to an isopropyl group attached to the C_{24} quaternary carbon atom, and the chemical shift of the methine proton of the isopropyl group, 2.83 ppm, showed the Z-configuration of the ethylidene substituent, as in citrostadienol and isofucosterol; in isocitrostadienol and fucosterol, having the E-configuration, the proton at C_{25} resonates at 2.20 ppm [5].

Thus, for the first time a compound belonging to the cycloartane series — 24-Z-ethylidenecycloartanol — has been isolated from sea buckthorn fruit.

REFERENCES

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