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STRUCTURE OF AN ACETYLENIC COMPOUND FROM *PANAX GINSENG*

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INTRODUCTION

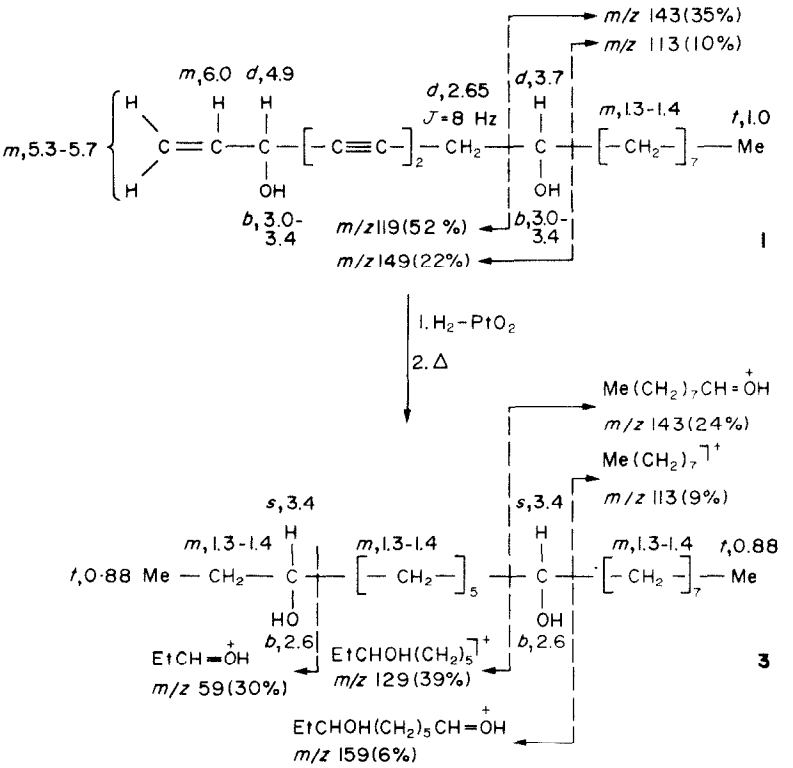
Two polyacetylenic alcohols have been isolated from *Panax ginseng* [1, 2]. Our investigations have led to the isolation of a new one; its structure is proposed on the basis of the NMR and high resolution MS data of the natural product and its hydrogenated derivative.

RESULTS AND DISCUSSION

From an ethereal fraction of a commercial water-alcoholic extract of *Panax ginseng* CA Meyer (obtained from Union of Herbs Industry "Herbapol", Poland), we have isolated an amorphous compound **1** ($C_{17}H_{26}O_2 \cdot H_2O$). Its IR spectrum showed the presence of hydroxy (3500–3300) acetylenic (2270) and vinyl (1600) cm^{-1} groups. In the UV only end absorption was observed; in its MS the parent ion was absent. Catalytic hydrogenation (five equivalents of hydrogen absorbed) led to a crystalline compound **2** which lost water of crystallization under high vacuum, resulting in **3**.

These data and analysis of the ^1H NMR spectrum allowed us to conclude that: (a) compound **1** contained an unbranched carbon skeleton with terminal methyl and vinyl groups; (b) two hydroxyl groups were present, one of them located between double and triple bonds at C-3 (the ^1H NMR signal of C<u>H</u>OH at δ 4.9 was shifted downfield); (c) the diacetylene moiety was attached to C-3 (unsaturation equivalent was 5; one vinyl group; absence in the ^1H NMR spectrum of protons for $\equiv C-C\underline{H}_2-C\equiv$; signals of the two protons in $\equiv C-C\underline{H}_2$ [3] present). These facts allowed us to ascribe the partial structure for compound **1** as

$$CH_2=CH-\underset{\underset{OH}{|}}{C}-C\equiv C-C\equiv C-; \quad (CH_2)_8; \quad (CHOH); \quad Me\cdot H_2O.$$



The location of the second hydroxy group was based on the analysis of the high resolution MS of the saturated compound **3** which should have the same carbon skeleton. A parent ion was absent when EI and CI methods were used; applying FD gave an M^+ at *m/z* 272 ($C_{17}H_{36}O_2$) which was in agreement with the elemental analysis and ^1H NMR data.

Our starting point was the analysis of ions $C_nH_{2n+1}O$ of the least value of *m/z* and ions C_nH_{2n+1} of the largest value of *m/z*. In aliphatic alcohols such ions can originate only as a result of α-fission to the C—OH bond. We found four such ions: $C_9H_{19}O$ and $C_8H_{17}O$ (C-8, C-9 fission); C_8H_{17} and $C_9H_{19}O_2$ (C-9, C-10 fission). The exact masses of the 38 ions examined confirmed the structures of all the fragments mentioned and allowed the assignment of C-9 for the position of the second hydroxy group. The structure of **3** is therefore proposed to be heptadeca-3,9-diol.

This structure is in agreement with the low resolution MS data. In the parent compound **1** there appeared ions at *m/z* 113 (10%) and 143 (35%) as found in the MS of **3**, but instead of ions 129 and 159 the corresponding ions at *m/z* 119 (52%) and 149 (22%) were generated. This indicated the identity in structures **1** and **3** of the fragment C-8 to C-17 and that the unsaturation (five equivalents) of **1** was in the fragment C-1 to C-7. Therefore we can ascribe the structure of heptadeca-1-en-4,6-diyn-3,9-diol for **1**.

The presence of three polyacetylenic alcohols of similar structures (panaxydol [2], falcarinol [1, 2, 4–7] and **1**) in *Panax ginseng* makes it probable that they arise from a mutual biogenetic pathway.

EXPERIMENTAL

^1H NMR spectra were measured on a 100 MHz spectrometer. The low resolution MS were taken with an ion source temp. of 290°, electron energy 70 eV, accelerating voltage 3.5 kV. The composition of all ions were established by high resolution measurements using the peak matching method and agreed with calculated values within the limits ±5 millimass units.

Isolation of **1**. 2 l. of the commercial ("Herbapol", Poland) 20% water–alcohol extract of *Panax ginseng* was concd under red. pres., below 35° to half of its volume and then extracted 20 × with hexane and 20 × with Et_2O. Combined ethereal extracts were evapd and the remaining oil was chromatographed on 200 g Si gel (100–200 mesh). From the hexane–EtOAc (1:1) fraction 320 mg of crude **1** was isolated. After crystallization from hexane, mp 80–85° (dec.). Yield: 0.015%, based on dry roots. (Found: C, 72.6; H, 10.4. $C_{17}H_{26}O_2 \cdot H_2O$ requires: C, 72.8; H, 10.0%).

Catalytic hydrogenation of **1**. 210 mg (0.75 mmol) of **1** in 10 ml EtOH was hydrogenated over 20 mg of PtO_2 under atm. pres. After 20 min the reaction was completed and 81 ml H_2 was absorbed. The catalyst was filtered off, the solvent removed and the residue crystallized from hexane. Yield of **2** = 202 mg (92%). Mp 81–82°. (Found: C, 70.3; H, 12.4. $C_{17}H_{36}O_2 \cdot H_2O$ requires: C, 70.3; H. 12.4%). 200 mg **2** was heated for 12 hr under high vac. Crystallization from hexane resulted in 170 mg (93%) of **3**. Mp 65–66°. (Found: C, 75.0; H, 13.2. $C_{17}H_{36}O_2$ requires: C, 74.9; H, 13.2%).

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