NOTE

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Sterols and Triterpenoids from the Fruit of *Cydonia oblonga* Miller[†]

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In the previous paper,[1] we reported the constituents of the essential oil of the quince fruit (*Cydonia oblonga* Miller). They were *trans*-α-farnesene and ethyl esters of some saturated and unstaturated fatty acids. In this paper, we wish to report the non-volatile constituents of this fruit.

The quince fruits were steam distilled to remove the essential oil, and the resulting fruits were, after drying, extracted with boiling benzene. The hot extract was set aside at room temperature over night and the precipitate (Fraction III) was collected by filtration. The filtrate was hydrolyzed and the hydrolysate was fractionated to the ether soluble neutral and acidic substances (Fraction I and Fraction II, respectively).

The methylated Fraction II was subjected to the silica gel column chromatography to give the mixture of fatty acid methyl esters, the constituents of which were studied by glc to reveal palmitic, oleic and linoleic acids.

Fraction I was subjected to the silica gel column chromatography to afford compound A, B, C, D and E.

The compound A obtained as a white solid showed the characteristic absorption bands of *n*-paraffin, and from its gas liquid chromatogram and GC–MS, it was confirmed that the compound A was the mixture of *n*-paraffins of C_{23}, C_{25}, C_{27} and C_{29}.

The compound B showed the typical bands and signals of the alcohol of $CH_3(CH_2)_xCH_2OH$ type in IR and NMR spectra. From the GC–MS, the compound B was confirmed to be the mixture of alcohols of C_{22}, C_{24}, C_{26} and C_{28}. The constituents of the compound A and B were resemble to that of the Portugese quince.[2]

The compound C and D, which were positive to the LB (Liebermann–Burchard) reaction, were identified as *β*-sitosterol[3] and saringosterol,[4] respectively, in comparison with physico-chemical data.

The compound E, which was also positive to LB reaction, was identified as uvaol in comparison with physico-chemical data of the synthetic sample obtained by reducing methyl ursolate by lithium alminum hydride.[5]

The IR spectrum of Fraction III showed the absorption bands of the hydroxyl and the carboxyl groups. The methylated Fraction III was fractionated to methyl esters of the compound F, G and H by the silica gel column chromatography.

The methyl ester of the compound F was positive to LB reaction and identified as methyl ursolate in comparison with physico-chemical data.[6]

The methyl esters of the compound G and H were obtained as colorless crystals of mp 186~7° and 218~9°C, respectively. From the IR, MS and NMR data, these compounds were considered to be triterpene acids. The detail of the structure of these compounds will be discussed elsewhere.

It is interesting that saringosterol which has been found in a marine agar is present in a land plant, the quince tree. It is noteworthy that ursolic acid is present in the quince fruit in such a large quantities (*ca.* 10 mg%).

EXPERIMENTAL

Material and isolation procedure

The fresh fruits of *Cydonia oblonga* Mill. (20 kg; harvested on November, 1975) were steam distilled to give 1.52 g of the essential oil.[1] After drying at room temperature for a week, the residual fruits were pulverized and extracted with the boiling benzene (5.4 liters) for 2 hr. The extracts were set aside at room temperature over night. After filtering the solid (3.96 g), the filtrate was evaporated to the syrup (11.82 g), 11.27 g of which was refluxed with 10% of ethanolic KOH for 2 hr. Working up by the usual method, the neutral substance (1.68 g) and acidic substance (7.35 g) were obtained.

Isolation of the compound A, B, C, D and E

The neutral fraction (1.67 g) was chromatographed on a silica gel column. The compound A (328 mg), B (446 mg), C (230 mg), D (72 mg) and E (32 mg) were obtained by eluting with the following solvent systems; hexane, benzene, benzene/ethylacetate (40: 1), benzene/ethylacetate (10: 1) and benzene/ethylacetate (5: 1) successively.

Properties of the compound A

IR ν_{max}^{KBr} cm^{-1}: 2840, 1450, 1370, 720. NMR (CCl_4) δ: 0.90 (6H, t, CH_3), 1.25 (*ca.* 50 H, m, CH_2).

Properties of the compound B

Mp 75~78°C (from MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1460, 1380, 1060, 720. NMR ($CDCl_3$) δ: 0.85 (3H, t, CH_3), 1.22 (*ca.* 45H, CH_2), 3.55 (1H, t, HO–C$\underline{H}$).

[†] Studies on the Chemical Constituents of Quince. Part II. (for Part I, see Reference 1)).

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GC–MS: m/e 308 (M^+-H_2O), m/e 336 (M^+-H_2O), m/e 364 (M^+-H_2O), 396 (M^+-H_2O). GLC t_R (min): 10.0 (2%*), 13.5 (25%), 17.0 (49%), 20.5 (21%).

Properties of the compound C

Mp 134°C (from EtOH). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 2900, 1640, 1440, 1365, 1060. NMR ($CDCl_3$) δ: 3.50 (1H, m, HO–C$\underline{H}$), 5.30 (1H, m, $\underline{H}$–C=C). $[\alpha]_D^{16}$: −36.0° (c=0.2, $CHCl_3$).

Properties of the compound D

Mp 160°C (from hexane/benzene 4 : 1). $[\alpha]_D^{20}$: −35.6° (c=0.21, $CHCl_3$). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 2900, 1640, 1460, 1380, 1060, 960, 920. NMR ($CDCl_3$) δ: 3.55 (1H, m, HO–C$\underline{H}$), 5.25 (1H, m, $\underline{H}$C=C), 5.08, 5.15 and 5.75 (3H, ABX, $\underline{H}$C=C$\underline{H}_2$).

Properties of the compound E

Mp 208~211°C (from MeOH). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 2900, 1460, 1380, 1100, 1050, 1000. NMR ($CDCl_3$) δ: 3.20~3.60 (3H, m, −C$\underline{H}_2$OH and C$\underline{H}$OH), 5.20 (1H, m, C=C$\underline{H}$–).

Synthesis of uvaol by reduction of methyl ursolate

The solution of methyl ursolate (300 mg) and $LiAlH_4$ (300 mg) in dry THF was refluxed for 6 hr. Working up by the usual method, it gave the colorless crystals (255 mg). Mp 221~2°C (from MeOH). $[\alpha]_D^{19}$: +69.6° (c=0.41, $CHCl_3$).

Isolation and identification of the fatty acids

Fraction II (1.2 g) was methylated by CH_2N_2 to give the yellow syrup (1.78 g), 190 mg of which was subjected to the silica gel column chromatography. From the benzene eluate colorless oil (fatty acid methyl esters, 92 mg) was obtained. GLC (DEGS column, 2m, 170°C), t_R (min): 2.5 (myristic, trace), 3.8 (palmitic, 26.6%*), 7.0 (stearic, 0.9%), 8.0 (oleic, 31.6%), 10.3 (linoleic, 40.9%), 14.5 (linolenic acid, trace).

Isolation of the compound F, G and H

Fraction III (3.96 g) was methylated by CH_2N_2 to give a white solid (4.0 g), 1.5 g of which was subjected to silica gel column chromatography. From the EtOAc/benzene (1 : 20) fraction the compound F methyl ester (725 mg) was obtained, and the compound G methyl ester (98 mg) from EtOAc/benzene (1 : 10) fraction and the compound H methyl ester (174 mg) from EtOAc/benzene (1 : 5) fraction respectively.

Properties of the compound F methyl ester

Mp 144~5°C (from MeOH), $[\alpha]_D^{19}$: +55.8° (c=0.42, $CHCl_3$). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 2850, 1730, 1455, 1380, 1200, 1050, 1038, 1000. NMR ($CDCl_3$) δ: 3.20 (1H, m, $\underline{H}$C–OH), 3.58 (3H, s, OMe), 5.22 (1H, m, $\underline{H}$–C=C).

Properties of the compound G methyl ester

Mp 186~7°C (from hexane/benzene 4 : 1). $[\alpha]_D^{18}$: +49.2° (c=0.50, $CHCl_3$). MS: m/e 486 (M^+). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3450, 2900, 1730, 1455, 1380, 1040, 1000. NMR($CDCl_3$) δ: 2.21 (1H, d), 3.38 (1H, d, $\underline{H}$C–OH), 3.95 (1H, m, $\underline{H}$C–OH), 5.20 (1H, m, $\underline{H}$–C=C).

Properties of the compound H methyl ester

Mp 218~7°C (from hexane/benzene 4 : 1). $[\alpha]_D^{20}$: +52.1° (c=0.17, $CHCl_3$). MS: m/e 486 (M^+). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 2900, 1730, 1450, 1380, 1050, 1030, 1000. NMR ($CDCl_3$) δ: 2.96 (d, $\underline{H}$C–OH, 1H), 3.60 (1H, m, $\underline{H}$C–OH).

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* The percentage of each compound was estimated by measuring the peak area.