Short Communication

Isolation and Identification of Novel Terpene Lactones from Quince Fruit (*Cydonia oblonga* Mill., Marmelo)Tomoyuki TSUNEYA, Masakazu ISHIIHARA,
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The fruit of the quince (*Cydonia oblonga* Mill.) has a powerful and characteristic sweet odor, however, it is not edible due to its very hard, tough and fibrous texture. Most of the fruit is used for marmalade and jelly. In Japan, the fruit is called the Japanese quince or marmelo.

A number of chemical constituents of quince fruit, such as organic acids, amino acids, sugars, flavonols, *etc.*, have been reported, while only few volatile constituents have been studied.¹⁾ Recently, Shimizu and Yoshihara²⁾ and Schreyen *et al.*³⁾ reported some of the volatile constituents of the fruit, but no compound responsible for the odor of the marmelo was isolated. Now, as described below, two compounds have been isolated from the volatiles of the fruit as the main components responsible for the characteristic odor of the marmelo and identified to be the 2,4-*cis*- and 2,4-*trans*-stereoisomers of 2,7-dimethyl-4-hydroxy-5*E*,7-octadienoic acid lactone (**I**). This is the first time these lactones have been isolated from a natural source.

I

Commercially available fresh fruit (11.75 kg), harvested in Nagano Prefecture in 1977, was sliced and subjected to steam distillation.

The distillate (23 kg) was saturated with sodium chloride and extracted with a mixed solvent (dichloromethane-*n*-pentane = 1/1, w/w, 14 kg) to give 0.658 g (*Y*: 0.0058%) of an essential oil having the strong sweet and fruity odor of the marmelo. The oil was indicated by GC analysis using a glass capillary column to contain two compounds as major components (the ratio in quantity, 4.5:5.5), each of which was isolated by chromatography on a silica gel column eluted with *n*-hexane-ether (30~20:70~80, v/v) and subsequent preparative GC on a PEG 20M 20% column (3 mm × 2 m, 180°C, TCD). The two isolated compounds were tentatively named compounds **A** and **B**, respectively. A single peak was observed at *Rt* 37.7 min on the gas chromatogram of **A** and at *Rt* 38.3 min on that of **B** (SF-96 glass capillary column, 0.28 mm × 40 m, temp., 70~220°C, after 5 min programmed at 3°C/min, FID).

The mass spectrum (GC-MS) of compound **A** [*m/e* (%): 166 (30, *M*⁺), 123 (28), 93 (31), 69 (33), 68 (100), 42 (35)] suggested the molecular formula of **A** to be C₁₀H₁₄O₂. In the IR spectrum of **A**, the following absorption bands were observed: $\nu_{\max}$ cm⁻¹: 3090 (double bond), 2983, 1778 (γ -lactone ring), 1610 (conjugated dien), 1168, 892 (endomethylene). The NMR spectrum (CCl₄, TMS) showed the presence of characteristic protons: a methyl proton attached to a methine carbon adjacent to a carbonyl group at δ 1.26 (3H, d, *J* = 7 Hz), an allylic methyl proton at δ 1.88 (3H, s), a methylene and a methine proton at δ 2.0~2.9 (2H, m and 1H, m), a methine proton adjacent to oxygen in the region of δ 4.9~5.25 (1H, m), an endomethylene proton at δ 5.11 (2H, s), and *trans*-olefinic protons at δ 5.73 (1H, dd, *J* = 6, 17 Hz) and at δ 6.45 (1H, d, *J* = 17 Hz).

From these spectral data, compound **A** can be proposed to have formula **I**. On the other hand, compound **B** showed quite similar spectral properties to those of **A**, as follows: MS *m/e* (%): 166 (30, *M*⁺), 123 (28), 93 (33), 69 (33), 68 (100), 42 (40). IR $\nu_{\max}$ cm⁻¹: 3090, 2980, 1777, 1611, 1170, 890. NMR $\delta_{\text{TMS}}^{\text{CCl}_4}$: 1.22 (3H, d, *J* = 6 Hz), 1.84 (3H, s), 2.27~2.85 (2H, 1H, m,

m), 4.58 ~ 5.08 (1H, m), 5.04 (2H, s), 5.63 (1H, dd, $J=7, 16$ Hz), 6.41 (1H, d, $J=16$ Hz). Consequently, compound **B** should be concluded to also have structure **I** and to be one of the stereoisomers of **A** in regard to the substituents on the γ -lactone ring. We propose that the isolated compounds should be named marmelo lactones **A** and **B**.

FIG. 1.

In order to confirm the above conclusion, **I** was synthesized by the method illustrated in Fig. 1. The condensation of 3-oxoglutarate with methallyl chloride formed ketoester **II** (bp 128 ~ 131°C/4 mmHg, Y : 81%), which was condensed with ethyl 2-bromopropionate in the presence of alcoholate and through sub-

sequent hydrolysis, reduction (NaBH₄) and cyclization with acid to give **III** (bp 128 ~ 133°C/10 mmHg, Y : 39%). After the isomerization of **III** to **IV** with p-TsOH, **IV** was converted to compound **V** through transformation of the double bond by chlorination. Dehydrochlorination with 1,8-diazabicyclo-[5,4,0]-7-undecene of **V** gave **I** (bp 130 ~ 134°C/6 mmHg, Y : 27.5%) which was a mixture of two isomers (mixing ratio, 4:6). The mixture was separated by preparative GC into the two stereoisomers, which were identified as marmelo lactones **A** and **B** on the basis of MS, IR and NMR data, respectively.

Both marmelo lactones **A** and **B** were isolated in such small amounts that further study of their stereochemistry could not be undertaken.

The GC-MS analysis was carried out with an SF-96 glass capillary column (0.28 mm $\times$ 40 m) on a Hitachi M-52. IR spectra were obtained with a JASCO IRA-1. NMR spectra were recorded on a Hitachi R-24 B.

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