**Communication**

**Formation Mechanism of 2,6-Dimethyl-2,6-Octadienes from Thermal Decomposition of Linalyl β-D-Glucopyranoside**

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Thermally decomposed products of (±)-linalyl β-D-glucoside were analyzed by GC and GC/MS. 2,6-Dimethyl-2,6-octadienes produced by mild pyrolysis of linalyl β-D-glucopyranoside under a vacuum were detected and characterized by MS and NMR spectroscopy. This suggests that 2,6-dimethyl-2,6-octadienes are produced during thermal decomposition of the glucoside via proton transfer from the anomeric position to C-6 in the aglycon moiety. A stable isotope labeling experiment directly indicated the new reaction mechanism.

**Key words:** thermal decomposition; linalool; terpene glucoside; flavor

To date, a large number of volatile terpenes and their glycosides have been found in plant leaves and flowers. Anderson et al. firstly isolated some glucosides of ionone-related compounds and vetispirane sesquiterpenes from tobacco leaves.1) Continuous study of terpene glycosides indicated the presence of several glycosides in Solanaceae.2) Recently, Yano et al.3) and Guo et al.4) have reported glycosides of volatile compounds in tea leaves and proposed their function to be aroma precursors. Interestingly, the glycos moiety of those glycosides was glucose, premerosever, or arabinoglucose. In addition, their concerted and aggressive work on tea aroma precursors indicated an important function of those glycosides with specific glycosidase.5)

On the other hand, aroma formation by thermal decomposition of those glucosides has not been investigated, except for tobacco products. The products of the thermal decomposition of menthol and vinyl glucosides have been investigated for use as sidestream aroma agents in cigarettes.6) More recently, synthetic and natural glucosides of ionone-related compounds such as 3-oxo-α-ionol have been tested for thermal decomposition to generate the dehydrated products of the aglycon moiety.2) These reactions might occur during food processing of several kinds of agricultural products. Due to the possible importance of these reactions, we investigated the thermal decomposition of the glucoside of linalool, which has an important aroma and is widely distributed in the plant kingdom. In this report, we show for the first time that 2,6-dimethyl-2,6-octadienes can form from (±)-linalyl β-D-glucoside during mild pyrolysis, and discuss the reaction mechanism.

To collect thermally decomposed products, the glucoside (10 mg) was dissolved in MeOH (0.5 ml) and coated on the bottom surface of a subliming flask by evaporating the MeOH in a vacuum. The flask was then evacuated to 46.7 hPa with a vacuum pump with closed two-way cocks. The temperature of the flasks was kept at 236 °C and the condenser was cooled to −10 °C. After heating for 5 min, the flask was cooled to room temperature and the products of thermal decomposition adhering to the surface of the condenser were detached with diethyl ether. Then the diethyl ether solution was analyzed as the thermally decomposed products of (±)-linalyl β-D-glucoside by GC and GC/MS. The thermally decomposed products of the glucoside consisted of 2,6-dimethyl-2,6-octadienes, together with linalool, limonene, and cis-ocimene, which were identified with authentic data. 2,6-Dimethyl-2,6-octadienes showed a peak at 8.39 min as 6Z isomer and a peak at 8.99 min as 6E isomer, coincident with a synthetic (6Z)- and (6E)-2,6-dimethyl-2,6-octadiene.7) This reaction yielded the same spectrum of product as did thermal decomposition of linalool, except for 2,6-dimethyl-2,6-octadienes.

Terpene glycoside, consisting of glucose, liberates an aglycon and forms levoglucosan during thermal decomposition, followed by dehydration. In our experiment, the reaction mechanism for linalool, limonene, and cis-ocimene is thought to be that linalyl β-D-glucoside liberates an aglycon with levoglucosan. Linalool is dehydrated to form cis-ocimene or cyclized to form...
limonene (Fig. 1). On the other hand, it is possible to think that formation of octadienes also occurs, and that linalyl \(\beta\)-D-glucoside is directly decomposed to octadienes with formation of gluconolactone (Fig. 2).

To investigate this reaction mechanism, deuterium labeled glucoside, \([1^{\text{a}}-2\text{H}] \, (\pm)\text{linalyl} \, \beta\)-D-glucopyranoside,\(^8\) was used. Thermal decomposition of \([1^{\text{a}}-2\text{H}] \, (\pm)\text{linalyl} \, \beta\)-D-glucopyranoside was done the same way as non-labeled and analyzed by GC–MS (Fig. 3). Both peaks for (6Z)- and (6E)-2,6-dimethyl-2,6-octadienes were identified by comparison with the non-labeled chromatogram, and showed ion peaks at \(m/z\) 139 (\(M^+\)) and 124 (\(M^+\) – \(\text{CH}_3\)). Deuterium enrichments of mono-deuteriated 2,6-dimethyl-2,6-octadienes A and B were determined to be 73.4% and 80.5% respectively, on the basis of the relative intensity of their \(M^+\) ions at \(m/z\) 139 to those of non-labeled compounds at \(m/z\) 138 and natural abundance of \((M + 1)^+\) ions at \(m/z\) 139 in non-labeled compounds.\(^9,10\) This result indicated that deuterium at H-1 in the glucose moiety was transferred to 2,6-dimethyl-2,6-octadiene during thermal decomposition. Further evidence of the reaction mechanism was obtained from an analysis of the decomposed glucose moiety. To find decomposed glucose moiety, the residue on the bottom surface of the flask was also analyzed after treatment with TMS chloride. GC–MS analysis of the TMS derived residue showed a peak for 2,3,4,6-tetra-O-TMS-glucono 1,5-lactone identical with those of an authentic sample. Thus, when linalyl \(\beta\)-D-glucoside is directly decomposed, it forms to octadienes with a formation of gluconolactone.

Such model studies might provide information pertaining to reaction mechanisms and to the nature of the compounds involved in pyrolytic formation in green tea. Octadienes have a citrus-like odor, which gives an important flavor to processed Japanese tea. Recently, this compound was found in oolong tea and houji-cha (a kind of Japanese tea).\(^11,12\) We think that this reaction might occur in the preparation of oolong tea and houji-cha. Further work is now under way to reveal the effect of stereochemistry at the C-3 position of the aglycon moiety.

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Fig. 1. Thermally Decomposed Products of (±)-Linalyl \(\beta\)-D-Glucoside.
(±)-\text{linalyl} \(\beta\)-D-glucoside liberates linalool and forms levoglucosan during thermal decomposition, and linalool is dehydrated to form cis-ocimene or cyclized to form limonene.

Fig. 2. Proposed Mechanism for Production of 2,6-Dimethyl-2,6-Octadiene from (±)-Linalyl \(\beta\)-D-Glucoside.
It is possible to think that the formation of octadienes also occurs, and that linalyl \(\beta\)-D-glucoside is directly decomposed to octadienes with formation of gluconolactone.

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References and Notes


7) 2,6-Dimethyl-2,6-octadiene. A solution of potassium $\text{t}$-butoxide (4.26 g, 37.96 mmol) in diethyl ether (10 ml) was dropped into an ice-cooled solution of ethyltriphenylphosphonium bromide (10 g, 26.94 mmol) in diethyl ether (20 ml) at 0°C for 10 min, and the reaction mixture was stirred at the same temperature for 2 h. 6-Methyl-5-hepten-2-one (2.65 g, 21.00 mmol) was dropped into the reaction mixture at 0°C for 10 min, and then quenched with $\text{H}_2\text{O}$ (50 ml). The organic layers were successively washed with brine, dried with $\text{MgSO}_4$, and concentrated in vacuo. The residue was subjected to chromatography on 15% AgNO$_3$ silica gel (100 g, eluted with hexane-diethyl ether 95:5), to separate (6Z)-2,6-dimethyl-2,6-octadiene (0.138 g, 10.00 mmol) and (6E)-2,6-dimethyl-2,6-octadiene (0.138 g, 10.00 mmol). NMR data were measured with a JNM-ECA400 spectrometer. (6Z)-2,6-dimethyl-2,6-octadiene, NMR $\text{C}_14\text{H}$ (CDCl$_3$): 1.47 (3H, dq, $J = 6.9, 1.8$ Hz, 8-H$_3$), 1.52 (3H, br.s, 6-H$_3$), 1.57–1.60 (6H, m, 1-H$_3$, 2-CH$_3$), 1.94–1.98 (4H, m, 4-H$_2$, 5-H$_2$), 5.02–5.05 (1H, m, 3-H), 5.11 (1H, qq, $J = 6.9, 1.4$Hz, 7-H$_2$); $\delta_\text{C}$ (CDCl$_3$): 13.1, 17.4, 23.3, 25.6, 26.8, 31.6, 119.0, 124.4, 131.2, 135.8, (6E)-2,6-Dimethyl-2,6-octadiene (0.138 g, 10.00 mmol). NMR data were measured with a JNM-ECA400 spectrometer. (6Z)-2,6-dimethyl-2,6-octadiene, NMR $\delta_\text{H}$ (CDCl$_3$): 1.47 (3H, dq, $J = 6.9, 1.8$Hz, 8-H$_3$), 1.52 (3H, br.s, 6-H$_3$), 1.57–1.60 (6H, m, 1-H$_3$, 2-CH$_3$), 1.94–1.98 (4H, m, 4-H$_2$, 5-H$_2$), 5.02–5.05 (1H, m, 3-H), 5.11 (1H, qq, $J = 6.9, 1.4$Hz, 7-H$_2$); $\delta_\text{C}$ (CDCl$_3$): 13.1, 17.4, 23.3, 25.6, 26.8, 31.6, 119.0, 124.4, 131.2, 135.8, (6E)-2,6-Dimethyl-2,6-octadiene (0.138 g, 10.00 mmol). NMR data were measured with a JNM-ECA400 spectrometer.
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4-H, $J = 7.8, 7.8$ Hz), 5.08–5.13 (1H, m, 3-H), 5.20 (1H, q, $J = 6.9, 1.4$ Hz, 7-H); $\delta_C$ (CDCl$_3$): 13.3, 15.6, 17.6, 25.6, 26.8, 39.8, 118.2, 124.4, 131.2, 135.7.

8) [1-$^2$H] ($\pm$)linalyl β-D-glucopyranoside. To a mixture of [1-$^2$H] 2.3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (2.13 g, 5.16 mmol prepared from [1-$^2$H]D-glucose, 99.9 atom %) and Hg(CN)$_2$ (3.91 g, 15.48 mmol) in dry MeCN (17.2 ml) was added (±) linalool (2.39 g, 15.46 mmol). The reaction mixture was then stirred at room temp. for 12 hr after which it was filtered through on celite followed by partitioning with EtOAc and water. The EtOAc layer was applied to SiO$_2$ column chromatography (eluted with hexane–EtOAc 4:1) to afford [1-$^2$H] (±)linalyl tetraacetyl-β-D-glucopyranoside (790 mg, 1.63 mmol, 31.58%). [1-$^2$H] (±)Linalyl tetraacetyl-β-D-glucopyranoside (760 mg, 1.57 mmol) was treated with 10 ml of the methanolic ammonia for 12 hr at room temperature to give [1-$^2$H] (±)linalyl tetraacetyl-β-D-glucopyranoside (0.43 mg, 1.36 mmol, 86.6%). FD-MS $m/z$: 317 (M$^+$$)$. The deuterium labeling enrichment of the product was calculated to be about 100% by NMR spectroscopy.


12) Identification of 2,6-dimethyl-2,6-octadienes in houji-cha (a kind of Japanese tea). Deionized hot water (80 $^\circ$C, 1 liter) was added to 60 g of houji-cha, the leaves were filtered using coarse filter paper after standing for 5 min, and steam distillation was performed under reduced pressure (40 $^\circ$C, 20 mmHg). The steam distillate (500 ml) was passed through a column packed with 10 g of Porapak Q (Waters). Adsorbed compounds were eluted with diethyl ether (50 ml), the elute was dried over anhydrous magnesium sulfate, and the solvent was removed with a rotary evaporator to about 2 ml in volume. Further concentration was carried out with a nitrogen stream to about 10 µl. 2,6-Dimethyl-2,6-octadienes were detected by GC and GC–MS from this concentrate.