Chapter 30

Natural Precursors of Thermally Induced C_{13} Norisoprenoids in Quince

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High resolution gas chromatographic (HRGC) and spectroscopic (MS; FTIR; ^{1}H-NMR) studies of quince fruit constituents revealed the occurrence of several free and glycosidically-bound precursors, which generate C_{13} norisoprenoids upon thermal treatment. 4-Hydroxy-7,8-dihydro-β-ionol was identified as a natural precursor of the isomeric theaspiranes, the major volatile constituents in quince fruit juice. Four thermally-induced megastigma-6,8-dien-4-ones were identified, and 4-hydroxy-β-ionol was established as their natural precursor. Sugar conjugates that play a principal role as antecedents of C_{13} norisoprenoids include glycosidically bound 3-oxo-α-ionol, which thermally produces megastigmatrienones. In addition, heat treatment of the conjugate of 3-hydroxy-β-ionol yields bicyclo[4.3.0]nonanes and 3,4-didehydro-β-ionol. The glycoside of 7,8-dihydrovomifoliol was previously substantiated to be thermally degraded to theaspirones.

Many interesting norisoprenoid aroma compounds have been identified in fruits, vegetables and in particular, tea (1) and tobacco (2). The formation of these flavor-significant components has been attributed to the degradation of higher molecular weight terpenoids, such as carotenoids, by biochemical and nonenzymic reactions in plant tissues (3). These degradations involve cleavage of C_9-C_{10}, C_8-C_9, C_7-C_8 and C_6-C_7 bonds of the polyene chain to produce compounds containing 13, 11, 10, and 9 carbon atoms, respectively. However, our knowledge about the immediate precursors of norisoprenoids and the reactions by which they are formed is rather scarce.

Several volatile C_{13} norisoprenoids have previously been identified in steam-distilled quince fruit oil, in which they are regarded to contribute to the overall flavor impression. These include isomeric theaspiranes, various bicyclononane derivatives, 3,4-didehydro-β-ionol, and isomeric megastigmatrienones and theaspirones (4,5). This report concerns the identification of additional norisoprenoids and their natural precursors in quince fruit.

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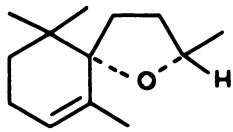
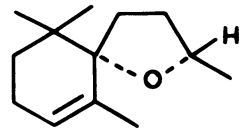
Isomeric Theaspiranes and their Natural Precursors

The spiroethers **1A** and **1B** are well-known constituents of several fruit aromas (6-12) and are widely used in the flavor industry (13).



1A

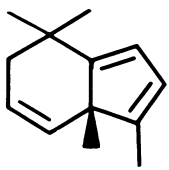


1B

They were identified among the main volatile constitutents of quince fruit juice after careful isolation at its natural pH (3.7), employing high-vacuum distillation/solvent extraction (HVD/SE) at 40°C. However, using fruit juice neutralized to pH 7.0 for flavor isolation, HRGC and HRGC-MS revealed only traces of these components (14). These results demonstrate that spiroethers **1A/1B** were originally not present in the intact fruit, but were formed at the natural pH of quince fruit juice after mild heat treatment from an unstable, less volatile precursor. This precursor was identified as 4-hydroxy-7,8-dihydro-β-ionol (4). Its synthesis from 4-oxo-β-ionol **2** as outlined in Figure 1, showed coincidence of HRGC and spectral data (MS, FTIR) with those of the constituent isolated from natural quince fruit (Winterhalter, P.; Schreier, P. J. Agric. Food Chem., in press). Prior to this, diol **4** had not been described in the literature. The mechanism of theaspirane formation from the natural precursor **4** can be considered to occur by prototropic dehydration of the corresponding allyl-1,6-diol, as previously described for monoterpene diols by Ohloff et al. (15), giving rise to tetrahydrofuran derivatives (Figure 2).

Bicyclo[4.3.0]nonanes, 3,4-Didehydro-β-ionol and their Natural Precursors

Upon employing the more rigorous simultaneous distillation-extraction (SDE) technique (100°C; pH 3.7) to isolate the quince fruit volatiles, the resulting aroma composition distinctly differed from that obtained by HVD/SE. After SDE the hydrocarbon **5**, the bicyclic alcohol **6** and 3,4-didehydro-β-ionol (**7**) were identified as



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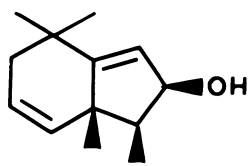

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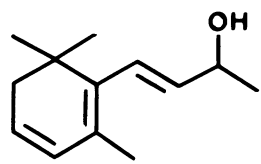

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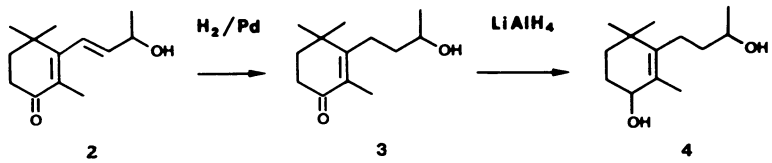


Figure 1. Synthesis of 4-hydroxy-7,8-dihydro-β-ionol (4) from 4-oxo-β-ionol (2) via 4-oxo-7,8-dihydro-β-ionol (3).

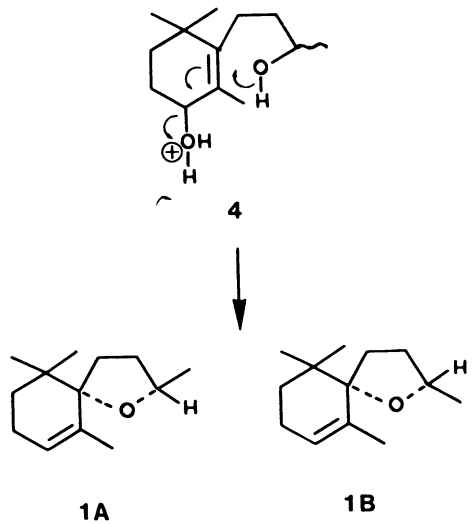
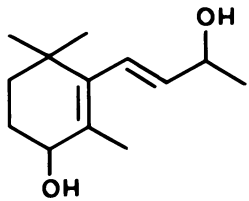


Figure 2. Proposed mechanism for theaspirane 1A/1B formation by prototropic dehydration of 4-hydroxy-7,8-dihydro-β-ionol (4) according to Ohloff et al. (Ref. 15).

major volatiles. In smaller amounts, several isomers of 5 with MW 174 and an isomer of alcohol 6 with MW 192 were detected.

Recently, Japanese researchers have demonstrated that the C_{13} norisoprenoid alcohol 7 has a key role as a flavor intermediate, but information about its natural precursor was not provided (4,5). Potential structures for the precursor of 7 comprise diols 8 and 9; in either case, simple dehydration can afford a double bond in the 3,4-position. Furthermore, the hydroxyl group of 7 could conceivably be glycosidically-bound.



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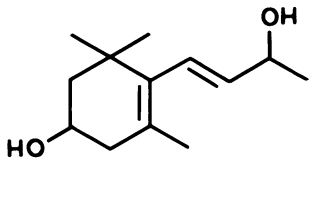

9

Diols 8 and 9, identified by us in quince fruit for the first time, were synthesized and subjected to thermal processing in model reactions (Winterhalter, P.; Herderich, M.; Schreier, P. J. Agric. Food Chem. in press). Accordingly, 4-hydroxy-β-ionol (8) was subjected to thermal degradation under SDE conditions (100°C; pH 3.7), and the results are outlined in Figure 3. In these model reactions, besides a minor quantity of previously-known norisoprenoids 5, 10A/10B and 11A/11B, the majority of degradation products (72%) consisted of the isomeric megastigma-6,8-dien-4-ones 12A-12D. These latter norisoprenoids have not been reported as yet in the literature. Isomer 12B, isolated in purified form by MPLC, showed a weak, long-lasting tobacco note with a cooling effect.

Dienones 12A-12D were also detected as trace components in quince fruit volatiles after SDE sample preparation. However, as shown in Figure 3, except for the low amount of hydrocarbon 5, the distribution of thermal degradation products from 8 did not correspond to the composition of the major C_{13} norisoprenoids 5-7 obtained after SDE of quince fruit juice. Consequently, diol 8 had to be excluded as their precursor.

In a further series of experiments, model reactions to thermally-degrade 3-hydroxy-β-ionol (9) were carried out. The results of these studies are represented in Figure 4. In these model reactions, compounds 5, 6 and 7 as well as unidentified isomers of 5 and 6 were all found in amounts very similar to the natural quince flavor composition obtained by SDE conditions. However, as shown in Figure 4, additional products were found comprising the megastigmatrienols 13, 14 and the tentatively-assigned bicyclic alcohol 15. These latter compounds were not detectable in quince fruit juice. Thus, the diol 9 came under question as a possible precursor.

One explanation for this surprising result is that the diol 9 is present in quince fruit in both the free and bound forms. To verify this, the glycosides in quince fruit were isolated by XAD

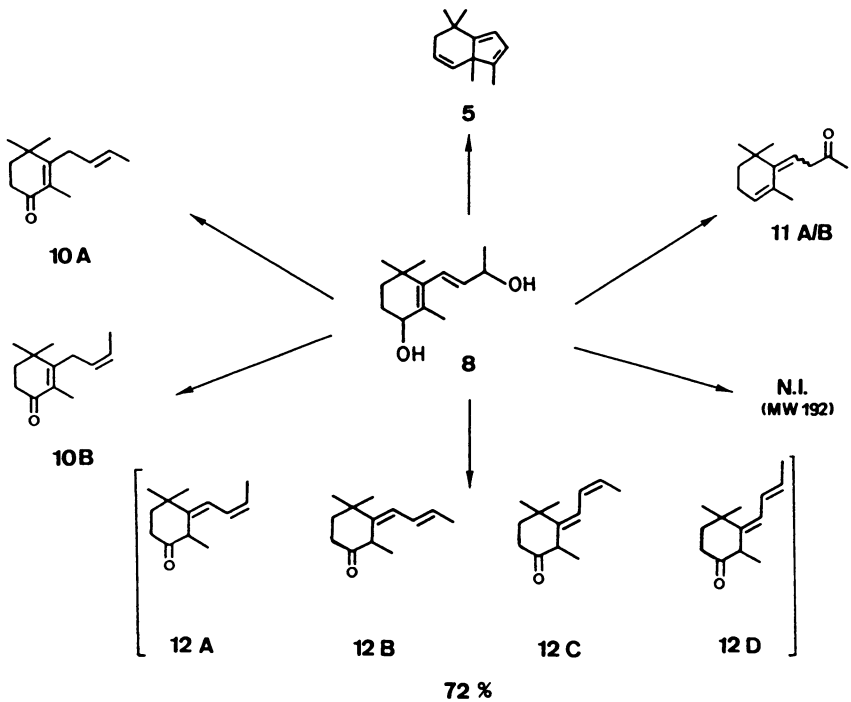

Figure 3. Structures of thermal degradation products of 4-hydroxy-β-ionol (8) under SDE conditions (100°C; pH 3.7). 5 = 2,2,6,7-tetra-methylbicyclo[4.3.0]nona-4,7,9(1)-triene; 10A/10B = E- and Z-megastigma-5,8-dien-4-ones; 11A/11B = isomeric retro-α-ionones; 12A-12D = isomeric megastigma-6,8-dien-4-ones; N.I. = not identified.

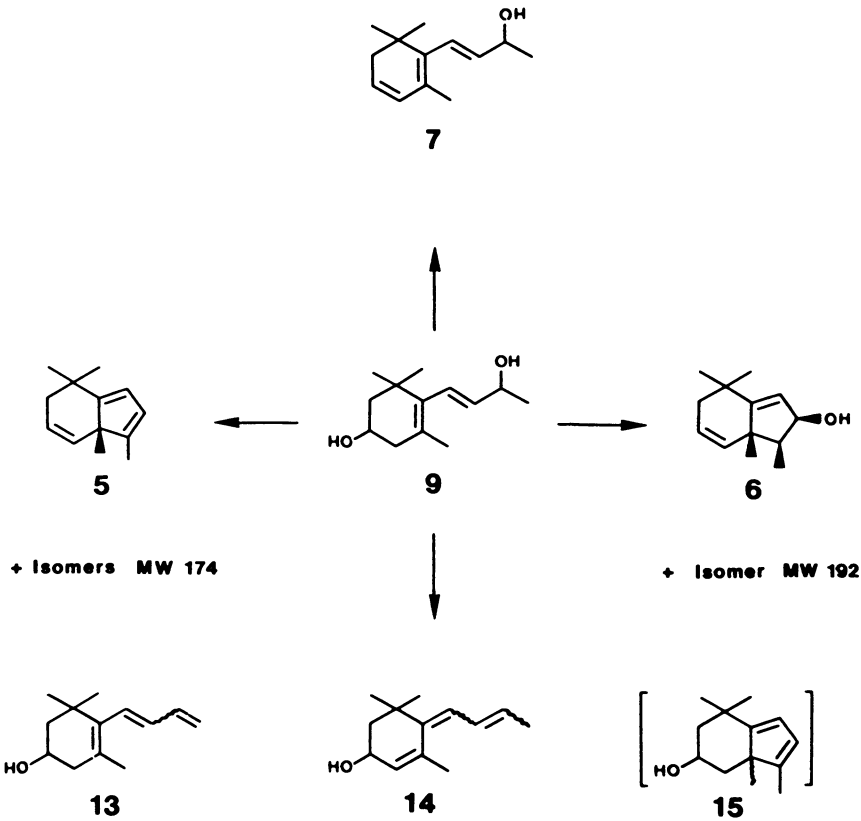

Figure 4. Structures of thermal degradation products of 3-hydroxy-β-ionol (9) under SDE conditions (100°C; pH 3.7). 5 = cf. Fig. 3; 6 = 2,2,6,7-tetramethyl-bicyclo- [4.3.0]nona-4,9(1)-dien-8-ol; 7 = 3,4-didehydro-β-ionol; 13 = megastigma-5,7,9-trien-3-ol; 14 = megastigma-4,6,8-trien-3-ol; 15 = 2,2,6,7-tetramethyl-bicyclo[4.3.0]nona-7,9(1)-dien-4-ol.

adsorption and methanol elution. The glycosidic extract was then subjected to SDE (100°C; pH 3.7) and the volatiles formed were analyzed by HRGC and HRGC-MS. The results obtained in this experiment are represented in Figure 5. First, it has to be emphasized that a similar composition of C_{13} norisoprenoid products was obtained as found after SDE treatment of quince fruit juice. In addition, marmelo ether (16) and marmelo lactone (17) were also identified. These results suggested that the thermally-induced C_{13} norisoprenoids found in quince fruit originated from a sugar conjugate of diol 9 as a precursor. To confirm this hypothesis, the glycosidic extract of quince fruit was further subjected to enzymatic hydrolysis using commercial emulsin as a glycosidase. This led to liberation of 3-hydroxy-β-ionol (9) as the major aglycone. In addition to 9, other glycosidically-bound C_{13} norisoprenoids were identified, including 3-hydroxy-β-ionone (18), 3-oxo-α-ionol (19), 3-hydroxy-7,8-dihydro-β-ionol (20), vomifoliol (21) and 7,8-dihydrovomifoliol (22) (Figure 6).

Megastigmatrienones and their Natural Precursors

Among the aglycones shown in Figure 6, 3-oxo-α-ionol (19) played a role as a precursor of other C_{13} norisoprenoids detected in quince fruit after SDE sample isolation. As outlined in Figure 7, the keto-alcohol 19 is known to be degraded to the isomeric megastigmatrienones 23A-23D and 24A/24B (16,17) after thermal treatment under acidic conditions.

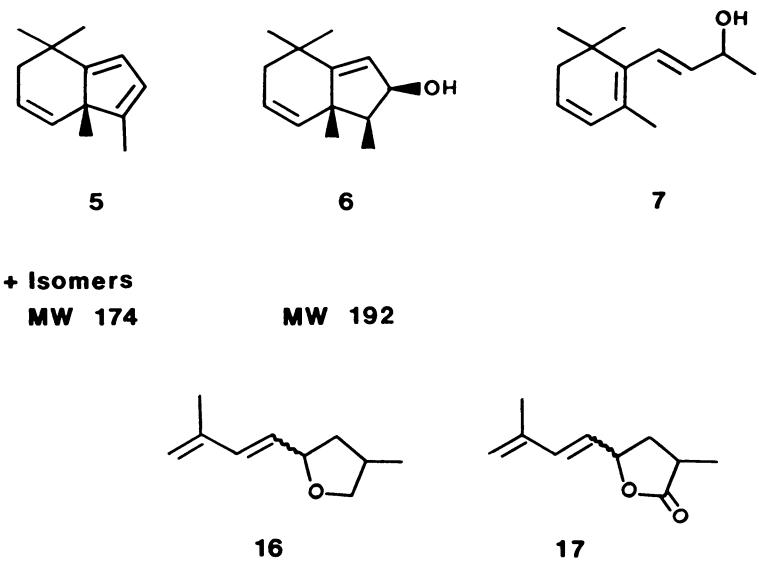

Figure 5. Major volatiles formed from glycosidic extract from quince fruit after SDE treatment (100°C; pH 3.7). 5, 6, 7 = cf. Fig. 4; 16 = marmelo ether; 17 = marmelo lactone.

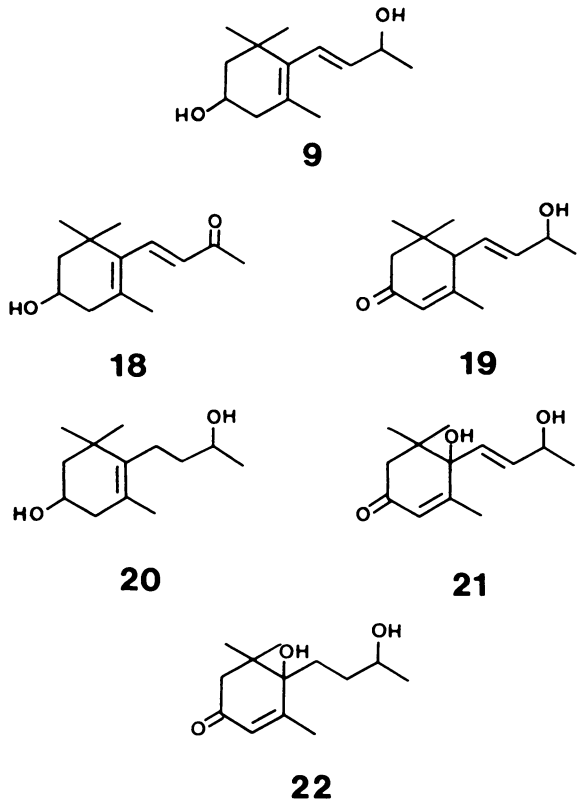

Figure 6. Structures of aglycones released from quince fruit extract after glycosidase (emulsin) treatment. 9 = 3-hydroxy-β-ionol; 18 = 3-hydroxy-β-ionone; 19 = 3-oxo-α-ionol; 20 = 3-hydroxy-7,8-dihydro-β-ionol; 21 = vomifoliol; 22 = 7,8-dihydrovomifoliol.

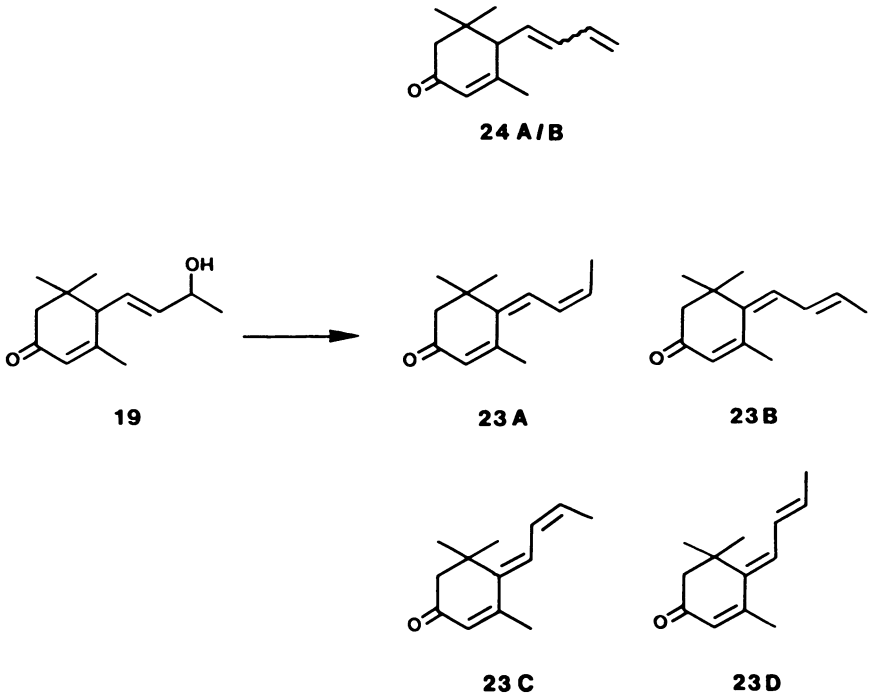

Figure 7. Structures of thermal degradation products of 3-oxo-α-ionol (**19**) under SDE conditions (100 °C; pH 3.7). **23A–23D** = isomeric megastigma-4,6,8-trien-3-ones; **24A/24B** = isomeric megastigma-4,7,9-trien-3-ones. (Redrawn from ref. 16 and 17.)

Isomeric Theaspirones and their Natural Precursors

Another C_{13} norisoprenoid aglycone in quince fruit, 7,8-dihydrovomifoliol (22) (cf. Figure 6), can be considered to be the precursor of theaspirones, which were previously found in steam-distilled quince fruit oil (4). As outlined in Figure 8, a synthetic sequence from α-ionone via dehydrovomifoliol (25) and vomifoliol (21) leads to 7,8-dihydrovomifoliol (22), from which the isomeric theaspirones **26A/26B** are formed after thermal treatment (18).

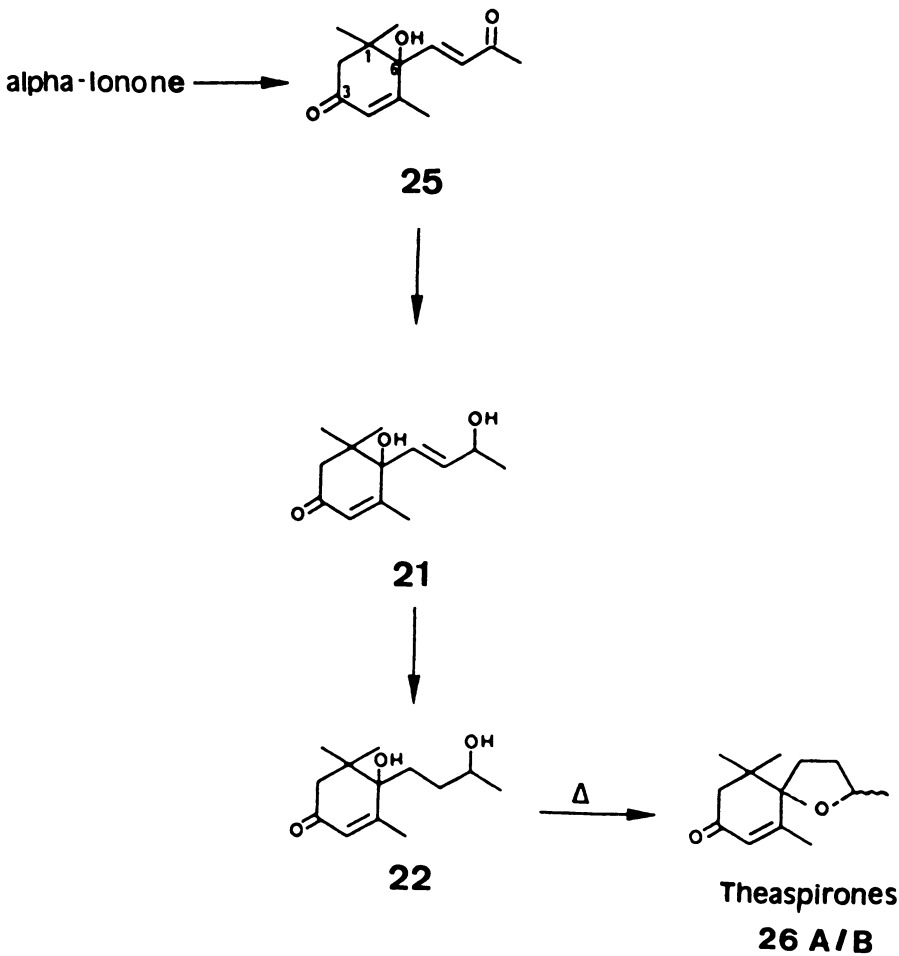

Figure 8. Synthesis of theaspirones **26A/26B** from α-ionone via dehydrovomifoliol (**25**), vomifoliol (**21**) and 7,8-dihydrovomifoliol (**22**). (Redrawn from ref. 18.)

Acknowledgments

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