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The Acid-catalyzed Isomerization of α-Ylangene and α-Ylangene Epoxide

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Upon treatment with dilute mineral acid, α-ylangene afforded two alcohols with amorphane carbon skeletons, 10β-hydroxyamorpha-4-ene (**16**) and 10α-hydroxyamorpha-4-ene (**17**). The carbonic acid-induced isomerization of α-ylangene epoxide yielded 3α-hydroxy-α-amorphene (**19**), 3α-hydroxy-δ-amorphene (**20**), and 3α,10α-dihydroxyamorpha-4-ene (**21**). The structures of these compounds were strictly determined, and the revised structure **16** of δ-cadinol proposed by Lin was shown to conflict with the results of the isomerization of α-ylangene and with the previously-reported conversion of α-copaene into δ-cadinol (**10**) and T-muurolol (**11**) under similar conditions.

As has been reported in a previous communication, some tricyclic sesquiterpene hydrocarbons containing a cyclopropane or a cyclobutane ring adjacent to a double bond in their molecule, such as α-cubebene (**1**), α-copaene (**2**), and α-ylangene (**3**), were easily isomerized by dilute mineral acid to give hydrocarbons and alcohols of the cadalene type.[1] Cadina-4,6(1)-diene (**4**), δ-cadinene (**5**), cadina-1,4-diene (**6**), cubenol (**7**), and epi-cubenol (**8**) were obtained from α-cubebene, and α-muurolene (**9**), δ-cadinene, δ-cadinol (**10**), and T-muurolol (**11**) from α-copaene. α-Ylangene afforded α-amorphene (**12**) and δ-amorphene (**13**), together with a small amount of oxygenated compounds of an unestablished structure.

Recently, Ohloff and his co-workers[2] performed the proton-induced isomerization of α-copaene epoxide in aqueous carbonic acid and reported the formation of three products, including (−)-3β-hydroxy-T-muurolol, which had previously been isolated from *Taiwania Cryptomerioides* by Lin.[3] These acid-catalyzed reactions are helpful in correlating these closely-resembling sesquiterpenoids of the cadalene type. In this paper, we wish to report the structure determination of compounds obtained from α-ylangene and α-ylangene epoxide by dilute-acid treatments.

Isomerization of α-Ylangene. α-Ylangene **3** was allowed to react with 0.1 N-sulfuric acid in aqueous acetone under reflux for three hours. Two sesquiterpene hydrocarbons, α-amorphene **12** and δ-amorphene **13**, were then isolated as the major components of the product (90%) in a ratio of 2 : 1, together with three oxygen-containing compounds (**15**—**17**) in a total amount less than 10% of the product. None of these

1) Y. Ohta, K. Ohara, and Y. Hirose, *Tetrahedron Lett.*, **1968**, 4181.

2) G. Ohloff and M. Pawlak, *Helv. Chim. Acta*, **53**, 245 (1970).

3) Y. H. Kuo, Y. S. Cheng, and Y. T. Lin, *Tetrahedron Lett.*, **1969**, 2375.

polar compounds isolated were identical with any material previously reported.

Compound (**15**) is an oil exhibiting the molecular ion at *m/e* 222 ($C_{15}H_{26}O$) and the base peak at *m/e* 161 in its mass spectrum. In its IR spectrum, no absorption maxima due to a hydroxyl or a carbonyl group or a double bond are observed, while the four strong bands in the region between 1145—1050 cm^{-1} suggest the presence of oxide linkage. Signals assignable to an isopropyl group at 0.86 and 0.88 (each 3H, doublets) and two methyl groups on the carbon-bearing ether-oxygen atom at 0.99 and 1.08 ppm were observed in its NMR spectrum. These spectral data led us to conclude that the structure of this oxide as **15**.

Compound (**16**) showed a molecular ion at *m/e* 222 ($C_{15}H_{26}O$) and an absorption maximum due to a hydroxyl group at 3650 cm^{-1}. Its NMR spectrum exhibited the signals attributable to an isopropyl group (0.88 and 0.96, two doublets), a methyl group on a carbon-bearing hydroxyl group (1.19), and an olefinic methyl group and a proton (1.68 and 5.47 ppm). On dehydration with thionyl chloride in pyridine, it afforded two hydrocarbons in a ratio of 1 : 1.5, which were confirmed to be α-amorphene **12** and δ-amorphene **13** respectively by comparing their IR spectra and retention times in glc with those of the authentic samples. These chemical and spectral proofs support the idea that this compound is an amorphene-type alcohol carrying the hydroxyl group at C–10 and the trisubstituted double bond at C–4, as is shown by its structure **16**.

Compound (**17**) also showed a molecular ion at *m/e* 222 ($C_{15}H_{26}O$) and a hydroxyl absorption band at 3300 cm^{-1}. Its NMR spectrum closely resembled that of **16**; 0.90 and 0.96 (an isopropyl group), 1.22 (a methyl group on a carbon-carrying hydroxyl group), 1.64 (3H) and 5.34 ppm (1H)(a trisubstituted double bond). The dehydration of this alcohol with thionyl chloride in pyridine furnished one major and two minor hydrocarbons; the main product (above 90%) was identified as α-amorphene, while the others were identified as γ-(**14**) and δ-amorphene. Thus, Compound **17** is probably an epimeric isomer of **16** in view of the configuration of the hydroxyl group at C–10. The configurations of the hydroxyl groups of these alcohols, **16** and **17**, may be supposed to be β-axial and α-equatorial respectively on the basis of the results of their dehydration reactions. It is generally accepted that the *trans*-antiparallel elimination of the water molecule from an alcohol occurs by means of the action of thionyl chloride in pyridine, and, in our case, one of the epimeric isomers carrying the α-equatorial hydroxyl group at C–10 can be expected to give α-amorphene as the main dehydration product, since only the β-hydrogen atom at C–9 is *trans*-antiparallel toward the hydroxyl group in the amorpha-4-ene skeleton. Thus, the **17** alcohol is determined to be 10α-hydroxy-amorpha-4-ene. In contrast, the configuration of the hydroxyl group of the **16** alcohol, which afforded α- and δ-amorphene in a comparable ratio, was reasonably decided to be β-axial, since the α-hydrogen atoms on both C–1 and C–9 satisfied this condition.

Isomerization of α-Ylangene Epoxide. The reaction of α-ylangene with monoperphthalic acid in the presence of anhydrous sodium carbonate afforded α-ylangene epoxide (**18**) in a good yield. On treatment with aqueous carbonic acid in the same way as has been reported by Ohloff,[2] the epoxide yielded two monoalcohols (**19**, **20**) and a diol (**21**). The diol was crystallized from the reaction-product mixture, while the others were purified by chromatography on a silica-gel column.

Compound **19** showed a molecular ion at *m/e* 220 ($C_{15}H_{24}O$) and its absorption maximum at 3350 cm^{-1}. In its NMR spectrum, the signals assignable to the following groupings are observed: an isopropyl group (0.92 and 0.95), two olefinic methyls (1.72) and protons (5.3 and 5.45), and a secondary hydroxyl proton (4.00 ppm, multiplet, $W_{1/2h}$ 21 Hz). The oxidation of **19** with manganese dioxide furnished an unsaturated ketone (**22**), $\nu_{C=O}$ 1670 cm^{-1}, which was chromatographically and spectroscopically identical with the authentic material obtained from α-amorphene by *tert*-butyl chromate oxidation.[4] Therefore, the secondary hydroxyl group was located at C–3 of the α-amorphene skeleton, and the structure of this alcohol was concluded to be 3-hydroxy-α-amorphene **19**.

Another mono-ol **20**, $C_{15}H_{24}O$ (M^+ 220), ν_{OH} 3350 cm^{-1}, exhibited the following NMR signals: 0.92 (6H, doublet, an isopropyl group), 1.62 and 1.70 (two olefinic methyls), 5.46 (an olefinic proton), and 4.10 ppm (1H, multiplet, $W_{1/2h}$ 20 Hz, a secondary hydroxyl proton). On the basis of these spectral data and the mechanism of this epoxide-cleavage reaction,[2] the structure of this alcohol was established as **20** except for the stereochemistry of the hydroxyl group at C–3.

The last compound obtained from the epoxide, needle crystals (mp 136 °C), showed a molecular ion at *m/e* 238 ($C_{15}H_{26}O_2$) in its mass spectrum. The spectral data showed the signals for an isopropyl group (0.92, 6H, doublet, 1380 and 1385 cm^{-1}), a trisubstituted double bond (3H at 1.71 and 1H at 5.36, 1660 and 840 cm^{-1}), a tertiary methyl group on a carbon-bearing hydroxyl group (singlet at 1.13), and a secondary hydroxyl group (1H multiplet at 4.18 ppm, $W_{1/2h}$ 19 Hz, 3400 cm^{-1}). On acetylation with acetic anhydride in pyridine at room temperature, it afforded a hydroxy acetate in an excellent yield (ν_{max} 3350, 1740 cm^{-1}). The secondary hydroxyl group was placed at the allylic position C–3, since it gave, on oxidation with manganese dioxide, an α,β-unsaturated hydroxy ketone (**23**), ν_{max} 3500, 1640 cm^{-1}; down-field-shifted olefinic methyl (1.77 ppm) and proton (6.55 ppm). Furthermore, the reduction of the mono-acetate of **21** with calcium in liquid ammonia[5] yielded a sole product which was identical in all respects with the **17** obtained from α-ylangene directly.

All of the allylic hydroxyl groups of **19**, **20**, and **21** can be expected to have the same configuration and

4) Y. Ohta and Y. Hirose, *Tetrahedron Lett.*, **1969**, 1601.
5) K. Takeda, K. Sakurai and H. Ishii, *Tetrahedron*, **27**, 6049 (1971).

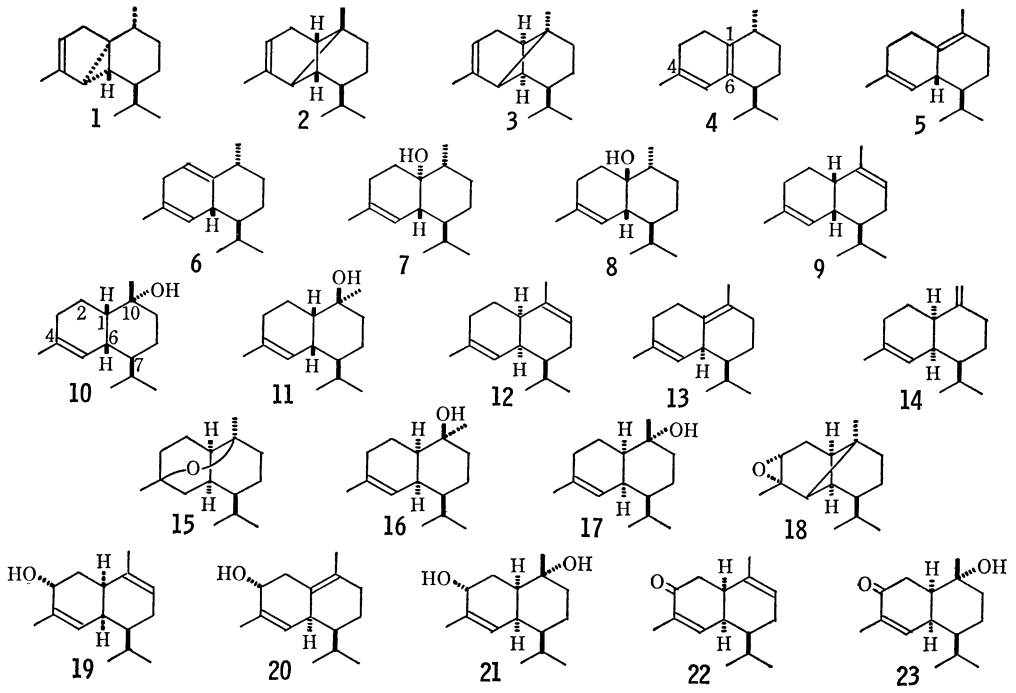

Fig.

can be decided as α-equatorial, since the observed $W_{1/2h}$ values of the secondary hydroxyl protons of these compounds are 21, 20, and 19 Hz respectively; the corresponding protons in the two tetrahydro derivatives obtained from **19** by catalytic hydrogenation also exhibited signals with $W_{1/2h}$ values of 21 and 25 Hz respectively in their NMR spectra. The stereochemistry of the tertiary hydroxyl group at C–10 of the diol **21** was reasonably decided to be α-equatorial on the basis of the reaction mechanism[2] and the successful conversion of **21** into **17**.

No compounds of the amorphane carbon skeleton with an oxygen functional group have yet been isolated from natural sources, but it is highly probable that some of them will be found in nature considering the stability and the biogenetical accessibility of such compounds.

Recently, Lin and his co-workers proposed a revised structure **16** for δ-cadinol that has an amorphane carbon skeleton.[6] However, this revised structure conflicts with the results that the acid-catalyzed isomerization of α-copaene afforded δ-cadinol and T-muurolol,[1] and that the dehydration of δ-cadinol yielded α- and γ-muurolene and δ-cadinene[6,7] 10β-Hydroxyamorpha-4-ene **16**, obtained from α-ylangene in our experiment, has a structure corresponding to their revised δ-cadinol, but it shows no identity with δ-cadinol in any other respect. Accordingly, we wish to propose again the previous structure **10** for δ-cadinol.

6) Y. T. Lin, Y. S. Cheng, and Y. H. Kuo, *ibid.*, **27**, 5337 (1971).

7) The dehydration of δ-cadinol with thionyl chloride in pyridine was carried out in our laboratory, too; α-muurolene (80%), γ-muurolene (15%), and δ-cadinene (5%) were identified as the dehydration products.

8) J. Pliva, M. Horak, V. Herout, and F. Šorm, "Die Terpene. I. Sesquiterpene," Akademie Verlarg, Berlin, (1960), S221.

Experimental

The melting points are uncorrected. The NMR spectra were taken on a Hitachi model R–20B NMR spectrometer (60 MHz), using TMS as the internal standard, and the chemical shifts are given in δ-values. The mass spectra were measured on a Hitachi RMU–6 mass spectrometer at 80 eV. The optical rotations were measured on a Perkin-Elmer model 141 polarimeter. The IR spectra were recorded on a Hitachi model EPI-G2 spectrophotometer. A Hitachi F6–D gas chromatograph fitted with a HB–2000 capillary column (0.25 mm × 45 m) was used for the analytical glc, and a Varian model 90–P gas chromatograph, for preparative purposes.

Isomerization of α-Ylangene. α-Ylangene was obtained from essential oil of the fruit of *Schisandra chinensis* as the main component of the oil. The oil was fractionally distilled under reduced pressure, and the fraction (bp 93—94 °C/9 mmHg) was chromatographed over neutral alumina (Merck, Grade II-III), using *n*-hexane as the solvent, to remove the oxygenated compounds. The hydrocarbon fraction thus obtained was further chromatographed over silica gel impregnated with 15% of silver nitrate, using *n*-hexane as the solvent, to give pure α-ylangene, which was identified by an IR spectrum comparison[8], $[\alpha]_D$ +55.6° (in chloroform). A solution of α-ylangene(3.5 g) in 2 l of 70% aqueous acetone containing 0.1 N sulfuric acid was heated under reflux for 3 hr. After cooling, the reaction mixture was neutralized with a 10% sodium bicarbonate solution, the solvent was then evaporated off to about a half volume under reduced pressure. The residue was extracted with ether, and the organic layer was washed with water and dried over anhydrous sodium sulfate. The product (3.0 g) was subjected to chromatographic separation on neutral alumina, and a hydrocarbon fraction (2.7 g) eluted with *n*-hexane and a fraction of oxygenated compounds (0.24 g) eluted with a 10% ether–*n*-hexane mixture were obtained. The hydrocarbon fraction was shown to consist of three compounds in

a ratio of 10 : 60 : 30 by analytical glc; the mixture was subjected to glc separation (Carbowax 20 M, 3/8″×20 ft column at 180 °C) to give α-ylangene, α-amorphene ($[\alpha]_D$ −127.6°, in chloroform) and, δ-amorphene ($[\alpha]_D$ +16.1° in chloroform) in order. The fraction of the polar compounds was shown to contain three compounds, (**15**), (**16**), and (**17**), in a ratio of 2 : 2.5 : 3, when purified by preparative glc (SE-30, 3/8″×10 ft column at 190 °C), they showed the following physical data. *Oxide (**15**)*; liquid, MS: *m/e* 222 (M^+, $C_{15}H_{26}O$, 72%) and 161 (base peak); IR: 1370, 1360, 1240, 1140, 1080, 1060, 1050, 1010, 1000, 985, and 970 cm^{-1}; NMR (CCl_4): 0.86 and 0.88 (each 3H, two doublets, J=6.0 Hz, $-CH(C\underline{H}_3)_2$), 0.99 and 1.08 (each 3H, singlet, $-O-\overset{|}{C}-C\underline{H}_3$). *10α-Hydroxyamorpha-4-ene (**16**)*; Oil, $[\alpha]_D$ −3.4°(*c*, 0.3 in chloroform), MS: *m/e* 222 (M^+, $C_{15}H_{26}O$), 189, 161(100%), 121, 120, 119, and 105; IR: 3650, 1660, 1390, 1080, 920, 865 and 780 cm^{-1}; NMR ($CDCl_3$): 0.88 and 0.96 (each 3H, two doublets, J=6.0 Hz, $-CH(C\underline{H}_3)_2$), 1.19 (3H, singlet, $HO-\overset{|}{C}-C\underline{H}_3$), 1.68 (3H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$) and 5.47 (1H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-\underline{H}$). *10β-Hydroxyamorpha-4-ene (**17**)*; mp 42 °C (recrystallized from petroleum ether), $[\alpha]_D$ −8.7° (*c* 0.5, chloroform), MS: *m/e* 222 (M^+, $C_{15}H_{26}O$), 204, 189, 164, 161, 121, and 95 (100%); IR: 3300, 1670, 1385, 1380, 1370, 1120, 1000, 940, 860, and 825 cm^{-1}; NMR ($CDCl_3$); 0.90 and 0.96 (each 3H, two doublets, J=6.0 Hz, $-CH(C\underline{H}_3)_2$), 1.22(3H, singlet, $HO-\overset{|}{C}-C\underline{H}_3$), 1.64 (3H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$) and 5.34 (1H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-\underline{H}$).

*Dehydration of 10β-Hydroxyamorpha-4-ene (**17**).* The alcohol **17** (7 mg) was dissolved in pyridine (1 ml) and treated with 30 mg of thionyl chloride at 0 °C for 15 min. The reaction mixture was poured into 30 ml of an ice-cold 10% sodium bicarbonate aqueous solution and extracted with 50% ether–*n*-hexane. The organic layer was washed with water and dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent gave 5 mg of an oily product which was subjected to glc separation; the α-amorphene (60%) and δ-amorphene (40%) thus obtained were identified by comparing their IR spectra with those of authentic samples.

*Dehydration of 10α-Hydroxyamorpha-4-ene (**16**).* A solution of 15 mg of **16** in 1 ml of pyridine was treated with thionyl chloride (75 mg) at 0 °C for 20 min. The subsequent usual work-up of the reaction mixture afforded 10 mg of a hydrocarbon mixture; after glc separation, α-amorphene (above 90%), γ-amorphene, and δ-amorphene were identified by comparing their IR spectra and R_t in glc with those of authentic samples.

Epoxidation of α-Ylangene. Into a solution of α-ylangene (5.0 g) in dichloromethane (100 ml) suspended in anhydrous sodium carbonate (3.9 g), and 8.4% ether solution of monoperphthalic acid (4.9 g) was stirred, drop by drop, at 0° C over a 15 min period. The reaction mixture was stirred at 4 °C for 18 hr. The precipitate was then filtered off using a glass filter, and the filtrate was washed with water and dried over anhydrous potassium carbonate. The oily product thus obtained (4.8 g) was subjected to column chromatographic purification over neutral alumina, using dichloromethane as the solvent, to give 4.5 g of α-ylangene epoxide **18**, which showed the following spectral data: prominent peaks at *m/e* 220 (M^+, $C_{15}H_{24}O$), 177 and 107 (100%) in its mass spectrum; absorption bands at 1380, 1375, 1370, 1095, 1060, 1020, 900, 840, 830, 820, and 720 cm^{-1} in its IR spectrum; NMR signals (CCl_4) at 0.86 (6H, doublet, J=5.4 Hz, $-CH(C\underline{H}_3)_2$), 0.88 (3H, singlet, $-\overset{|}{C}-C\underline{H}_3$), 1.29 (3H, singlet, $-\overset{|}{C}(O)-\overset{|}{C}-C\underline{H}_3$), 2.10 (1H, singlet, $\underline{H}C-\overset{|}{C}(O)-\overset{|}{C}-$), and 2.86 (1H, broad peak, $-\overset{|}{C}(O)-\overset{|}{C}-\underline{H}$).

Isomerization of α-Ylangene Epoxide. α-Ylangene epoxide (2.0 g) was added to a solution of dry ice (4 g) dissolved in 80 ml of freshly-distilled water. The mixture was shaken vigorously using a mechanical shaker for 20 hr at room temperature. The subsequent extraction of the reaction mixture with 300 ml of ether, drying over anhydrous sodium sulfate, and evaporation of the solvent afforded 1.8 g of a viscous oil which was stored, after the addition of 10 ml of an ether–*n*-hexane mixture (1 : 2), in a refrigerator overnight to deposit needle crystals of the diol **20**. The crystals (310 mg) were then filtered off and recrystallized from 50% ether in *n*-hexane; mp 136.0—136.5 °C, $[\alpha]_D$ +32.6° (*c* 0.3, chloroform), IR: 3400, 1660, 1415, 1385, 1380, 1120, 1040, 1025, 950, 905, and 840 cm^{-1}; MS; *m/e* 238 (M^+, $C_{15}H_{26}O_2$), 220, 202, 177 and 159 (100%); NMR ($CDCl_3$): 0.87 and 0.93 (each 3H, two doublets, J=6.0 Hz, $-CH(C\underline{H}_3)_2$, 1.13 (3H, singlet, $HO-\overset{|}{C}-C\underline{H}_3$), 1.71 (3H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 4.18 (1H, broad peak, $W_{1/2h}$ 19 Hz, $HO-\overset{|}{C}-\underline{H}$) and 5.36 (1H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-\underline{H}$). Found: C, 75.84; H, 10.88%. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00%.

The mother liquor was subjected to column chromatography over silica gel; 3α-hydroxy-δ-amorphene **20** (400 mg) and 3α-hydroxy-α-amorphene **19** (1.0 g) were then obtained by elution with 20% ether in *n*-hexane. *3α-Hydroxy δ-amorphene (**20**)*, oil, $[\alpha]_D$ +61.7° (*c*, 0.5 in chloroform), showed the following spectral data: IR: 3350, 1660, 1385, 1370, 1040 and 840 cm^{-1}; NMR ($CDCl_3$): 0.92 (6H, doublet, J=6.0 Hz, $-CH(C\underline{H}_3)_2$), 1.62 (3H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 1.70 (3H, doublet, J=2.5 Hz, $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 4.10 (1H, multiplet, $W_{1/2h}$ 20 Hz, $HO-\overset{|}{C}-\underline{H}$), and 5.46 (1H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-\underline{H}$). *3α-Hydroxy-α-amorphene (**19**)*, oil $[\alpha]_D$ −69.9° (*c*, 1.4 in chloroform), showed the following spectral data: IR: 3350, 1660, 1385, 1370, 1050, 1015, 850, 830, and 785 cm^{-1}; NMR ($CDCl_3$): 0.92 and 0.95 (each 3H, two doublets, J=6.0 Hz, $-CH(C\underline{H}_3)_2$), 1.72 (6H, finely-split multiplet, two olefinic methyl groups), 4.00 (1H, broad peak, $W_{1/2h}$ 21 Hz, $HO-\overset{|}{C}-\underline{H}$), 5.3 (1H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-\underline{H}$), and 5.4 (1H, broad peak, $-\overset{|}{C}=\overset{|}{C}-\underline{H}$).

*Oxidation of 3α-Hydroxy-α-amorphene (**19**).* To a solution of **19** (300 mg) in 50 ml of dichloromethane, manganese dioxide (3 g) was added; the mixture was then sitrred for 3.5 hr at room temperature. The subsequent filtration of the reagent and evaporation of the solvent gave 250 mg of an oily product. A pure sample obtained by glc separation (Carbowax 20 M, 3/8″×5 ft column at 180 °C) showed IR bands at 1670, 1380, 1370, 1110, 1095, 940, 900, and 825 cm^{-1}. This α,β-unsaturated ketone was identified with the authentic α-amorphene-3-one **22** obtained from α-amorphene by *tert*-butyl chromate oxidation by comparing their IR spectra, R_f on tlc and R_t in glc.

*Oxidation of the Diol (**21**).* Manganese dioxide (350 mg) was added to a solution of the diol **21** (50 mg) in dichloromethane (10 ml), the mixture was then stirred for 3 hr at room temperature. The usual work-up of the reaction mixture afforded crystals of α,β-unsaturated hydroxy ketone

23 (45 mg), which were then recrystallized from *n*-hexane; mp 129.5—130.5 °C; IR: 3500, 1640, 1408, 1375, 1365, 1110, 940, and 900 cm^{-1}; NMR ($CDCl_3$): 0.95 and 1.03 (each 3H, two doublets, J=6.0 Hz, $-CH(C\underline{H}_3)_2$), 1.00 (3H, singlet, $HO-\overset{|}{\underset{|}{C}}-C\underline{H}_3$), 1.77(3H, broad singlet, $-CO-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), and 6.55 (1H, broad singlet, $\underline{H}C=\overset{|}{C}-\overset{|}{C}=O$).

*Acetylation of the Diol (**21**).* The diol **21** (145 mg) was treated with dry pyridine (5 ml) and acetic anhydride (1 ml) at room temperature for 5.5 hr. The reaction mixture was poured into a dilute sodium bicarbonate solution and extracted with ether. The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated to give crude mono acetate (140 mg), which was then recrystallized from *n*-hexane; mp 117—118 °C, IR: 3275, 1740, 1250, 1125 and 1015 cm^{-1}; NMR ($CDCl_3$): 0.95 and 0.90 (each 3H, two doublets), $-CH(C\underline{H}_3)_2$, 1.19 (3H, singlet, $HO-\overset{|}{\underset{|}{C}}-C\underline{H}_3$), 1.62 (3H, broad peak, $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 2.05 (3H, singlet, $C\underline{H}_3COO-$), 5.45 (1H, multiplet, $AcO-\overset{|}{\underset{|}{C}}-\underline{H}$), and 5.60 (1H, broad singlet, $-\overset{|}{C}=\overset{|}{C}-\underline{H}$). Found: C, 72.75; H, 10.02%. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06%.

Reduction of the Diol Monoacetate. A solution of the monoacetate (85 mg) in toluene (3 ml) was stirred, drop by drop over a 15 min period, into a solution of calcium (0.8 g) in liquid ammonia (40 ml) at −70 °C. After the subsequent addition of ammonium chloride (3 g) to the mixture, the ammonia was evaporated. Water (150 ml) was added to the residue, and the residue was extracted with ether; the extract was washed with water dried over anhydrous sodium sulfate. The crude product was shown by tlc to contain almost a sole component, which was purified by glc separation (SE-30, 3/8″×10 ft column at 190 °C). The IR and NMR spectra, R_t in glc and R_f on tlc, of this reduction product were shown to be identical with those of 10α-hydroxyamorpha-4-ene **17**.