[Chem. Pharm. Bull. 16(6)1081—1087(1968)]

UDC 581.19 : 547.597.02 : 582.583

Structure of Zederone[1)]

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(Received October 4, 1967)

From zedoary, *Curcuma zedoaria* (Zingiberaceae), has been isolated a new sesquiterpenic keto-dioxide, zederone. Chemical and physicochemical studies of it and its derivatives permit the allocation of the structure I to it.

The crude drug zedoary, used chiefly as an aromatic stomachic, is prepared from the rhizome of *Curcuma zedoaria* Roscoe (Zingiberaceae), a perennial herb indigenous to or cultivated in tropical Asia. Although some work has been previously carried out on its components,[3)] further investigation of the crude drug seemed warranted and led to the isolation of the new sesquiterpenoids-curcumol,[4)] curcumenol,[5)] curdione,[6)] and curcolone.[7)] Further survey resulted in the isolation of a new sequiterpenic keto-dioxide which we have named zederone; the present paper describes in full detail the evidence which leads to the proposal of structure I for this substance.[8)]

Zederone, mp 153.5—154°, has the molecular formula $C_{15}H_{18}O_3$ as shown by elemental analysis and mass spectrometry.

The unsaturated character of zederone was first indicated by its nuclear magnetic resonance (NMR) spectrum which exhibited a one-proton quadruplet with additional fine splittings at 7.07 ppm and a three-proton doublet at 2.10 ppm. These line positions are indicative of an α-hydrogen and a β-methyl of a furan, respectively. Since the coupling constant (1.3 cps) measured for these two signals precludes a possible substitution pattern of the furan nucleus (*i.e.*, α-H and β'-CH_3), the presence of a trisubstituted furan system as in the part formula A (*i.e.*, an α-H and the vicinal β-CH_3) is deduced. In accordance with these spectral properties, zederone gave positive color tests for a furan moiety such as vanillin-hydrochloric acid, pine stick, Ehrlich, and Liebermann-Burchard reaction. The third ethylenic linkage was indicated by the presence of one vinyl proton signal at 5.47 ppm and one vinyl methyl signal at 1.60 ppm, both of which were spin-coupled with each other ($J=1.4$ cps); these chemical shifts suggested ruling out the possibility of any conjugation. Chemical evidence for the presence of the unconjugated ethylenic linkage was obtained by oxidation with perbenzoic acid to give

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1) This paper constitutes Part XXIII in the Tohoku University series on Sesquiterpenoids. Preceding paper, Part XXII, H. Hikino, Y. Tokuoka, Y. Hikino, and T. Takemoto, *Tetrahedron*, **24**, 3147 (1968).

2) Location. *a) Kita-4-bancho, Sendai. b) Palo Alto, California.*

3) For a historical background of early work, see E. Gildemeister and F. Hoffmann, "Die Ätherischen Öle," Vol. IV, Akademie Verlag, Berlin, 1956, p. 477.

4) H. Hikino, K. Meguro, Y. Sakurai, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **13**, 1484 (1965); *ibid.*, **14**, 1241 (1966).

5) H. Hikino, Y. Sakurai, S. Numabe, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **16**, 39 (1968).

6) H. Hikino, Y. Sakurai, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **14**, 1310 (1966); *ibid.*, **15**, 1390 (1967).

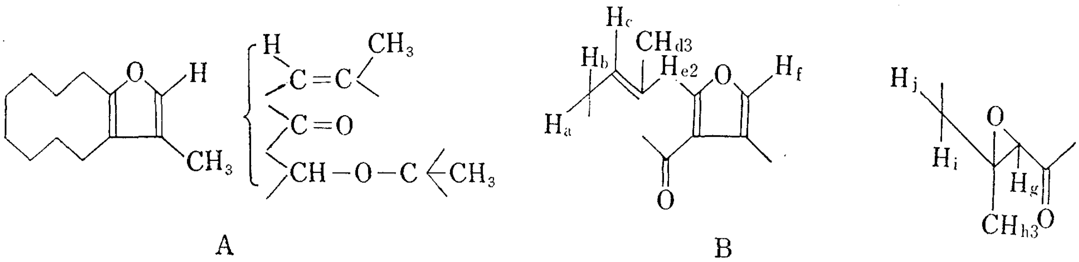
7) H. Hikino, Y. Sakurai, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **15**, 1065 (1967); *ibid*, **16**, 827 (1968).

8) Part of the material contained herein formed a preliminary communication *Chem. Pharm. Bull.* (Tokyo), **14**, 550 (1966).

the epoxide (II). Furthermore, catalytic hydrogenation over Adams' catalyst in methanol resulted in the saturation of the isolated double bond yielding a dihydro-derivative (III) which was considered to be a mixture of the epimers with respect to the carbon attached to the newly formed secondary methyl group, since its NMR spectrum exhibited each pair of signals which were required for the postulated structure III.

Our next endeavor was to confirm the nature of the three oxygen atoms present in zederone which could be accommodated as follows. The first one accounted for the furan system as described above. The second one is identified from an infrared band at 1661 cm^{-1}, assigned to an α,β-unsaturated ketone which must be part of the furoyl system because of the known unconjugated nature of the third ethylenic bond (*vide supra*). In agreement with this, zederone on lithium aluminum hydride reduction gave the alcohol (IV) which on oxidation with manganese dioxide regenerated the original ketone, zederone, indicating that no change had taken place during the reduction in the other part of the molecule. On catalytic hydrogenation over Adams' catalyst in methanol the alcohol (IV) gave the dihydro-alcohol (V), which was acetylated with acetic anhydride in pyridine to give the dihydro-acetate (VI). The third oxygen must be present as an oxide, since the infrared spectrum of zederone lacks hydroxyl bands and that of the mono-ol (IV) lacks carbonyl bands, while the NMR spectrum of zederone has a three-proton resonance at 1.33 ppm arising from a methyl on carbon carrying an oxygen and a one-proton signal at 3.78 ppm originating from a hydrogen on carbon bearing an oxygen.

The presence of these functional groups and the molecular formula require that zederone possesses a ten-membered monocarbocyclic skeleton as indicated in part formula A.



A B C

Chart 1

The environment of the third ethylenic linkage as in partial formula B was deduced from NMR data. The vinyl hydrogen (H_c) occurs as a broad quadruplet at 5.47 ppm (J_1 $=10.9$, $J_2=4.3$ cps), demonstrating its coupling with the adjacent methylene (H_a and H_b). The methylenic hydrogens (H_{e2}) have almost identical chemical shifts (3.69 and 3.72 ppm) in deuteriochloroform, but are clearly visible as an AB quadruplet ($J=16.5$ cps) with additional fine splittings at 3.28 and 3.39 ppm in benzene solution. Double resonance experiments revealed that the methylene (H_{e2}) signal is only weakly coupled with the H_{d3} ($J_1=0.5$, $J_2=0.5$ cps), H_c ($J_1=0.9$, $J_2=0.9$ cps), and H_f ($J_1=0.5$, $J_2=0.3$ cps). This fact shows that the methylene ($-CH_{e2}-$) is next to the third double bond and that the second carbon adjacent to this methylene is also quarternary. There are only three possibilities for placing the second quaternary carbon α to the methylene grouping ($-CH_{e2}-$) judging from the formula A. The direct linkage of the quaternary carbon in a $CH_3-C\lessdot O-$ system to the methylene ($-CH_{e2}-$) was eliminated by the strongly deshielded chemical shifts (3.69 and 3.72 ppm) of the methylene (H_{e2}) and, furthermore, by violation of the isoprene rule (*vide infra*). Second, the placement of the carbonyl group adjacent to the methylene group ($-CH_{e2}-$) was also excluded by the fact that the methylene (H_{e2}) signal in the alcohol (V) showed no coupling with the hydrogen on carbon bearing the hydroxyl group. It follows that the furan system must be adjacent to the methylene group ($-CH_{e2}-$) and this environment reasonably reflects the deshielded chemical shifts of the methylenic protons (H_{e2}). Further, substitution of the methylene group ($-CH_{e2}-$)

at the α'-position of the furan ring was suggested by the observed couplings ($J_1=0.5$, $J_2=0.3$ cps) of the α-hydrogen of the furan with the methylene hydrogens (H_{e2})[9]. In contrast to zederone and the alcohol (IV), the epoxide (II) exhibited the methylene (H_{e2}) signal as a quadruplet in an AB spectrum at 2.81 and 3.71 ppm ($J=16.9$ cps) in deuteriochloroform; this is due to epoxidation of the double bond rendering the chemical shifts of the methylene protons (H_{e2}) quite different.

This then completes the substitution pattern of the furan ring because the remaining (*i.e.*, β-) position must have a carbonyl adjacent to it as previously discussed. In agreement, the methylene (H_{e2}) signal of the alcohol (IV) is shifted to a higher field (both 3.48 ppm), as compared with those (3.69 and 3.72 ppm) in zederone, demonstrating that the methylene was situated within the magnetic effect due to the anisotropy of the carbonyl group in zederone, a fact which was also consistent with the postulated assignment B.

Substitution of the carbonyl group at the β'-position of the furan as in formula B was further confirmed by an additional NMR study of zederone which gave the information about the relative situation of the carbonyl and the methyl group attached to the β-position of the furan. Thus, the methyl resonance occurs at 2.10 ppm in deuteriochloroform, whereas it occurs at 2.14 ppm in benzene solution. The observed value (-0.04 ppm) of the solvent-induced shift, on passing from deuteriochloroform to benzene solution, is in agreement with the location of the furyl methyl group as situated at the β-*cis* position in an α,β-unsaturated carbonyl system forming an S-*cis* conformation.[9,10]

The conjugation of the epoxide function with the furoyl group, as shown in partial formula C, was established by the following NMR evidence. The methyl (H_{h3}) signal was found to be split by the coupling constant 0.8 cps. This was shown to be due to the long range coupling with one (H_i) of the methylenic hydrogens at *ca.* 0.98 ppm. The hydrogen (H_g) signal occurs as a singlet showing no sign of spin coupling with any protons. Of the possible arrangements of the oxide linkage, all except one, shown in part formula C, can be immediately dismissed since they would require some splitting of the methine proton (H_g) signal. The low shift (3.78 ppm) of the hydrogen (H_g) as a hydrogen in an epoxide ring is apparently due to the effect of the adjacent carbonyl group. If this is indeed the case, the hydrogen (H_g) signal should move towards a high field when the carbonyl group is converted into a hydroxyl group, since the shielding effect of the carbonyl group will be eliminated. In reality, the signal (3.78 ppm) of the hydrogen (H_g) in zederone moved upfield to 2.94 ppm in the alcohol (IV), 3.31 ppm in the dihydro-alcohol (V), and 3.22 ppm in the dihydro-acetate (VI). These signal positions are compatible with those of α-protons of epoxy-rings, also confirming the presence of the epoxide system in zederone. The coupling between the hydrogen (H_g) and the newly formed hydrogen (H_k) on carbon bearing the hydroxyl group must be anticipated in these cases. However, the hydrogen (H_k) signal of the alcohol (IV) appeared as a somewhat broadened peak even after addition of deuterium oxide, and the hydrogen (H_g) signal could not be observed clearly because of overlapping of the signal with that arising from the vinyl hydrogen (H_c). Therefore, exact assignment of the coupling between these signals (H_g and H_k) could not be performed in the alcohol (IV). On the other hand, in the dihydro-alcohol (V) and the dihydro-acetate (VI), the signal patterns of the α-hydrogens (H_g) of the epoxy-rings and of the hydrogens (H_k) on carbons attached to the oxygen functions were both doublets ($J=2.2$ and 1.9 cps, respectively) with no other spin-couplings, indicating the presence of the partial structure C in zederone.

The combination of the partial structures B and C, and the skeleton A leaves only one possible formulation I for zederone.

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[9] H. Hikino, unpublished data.

[10] C.J. Timmons, *Chem. Commun.*, 576 (1965).

Dehydrogenation of the alcohol (IV) with palladium-charcoal yielded linderazulene (VII), demonstrating that the skeleton obeys the isoprene rule; *viz.*, zederone has the germacrane skeleton.

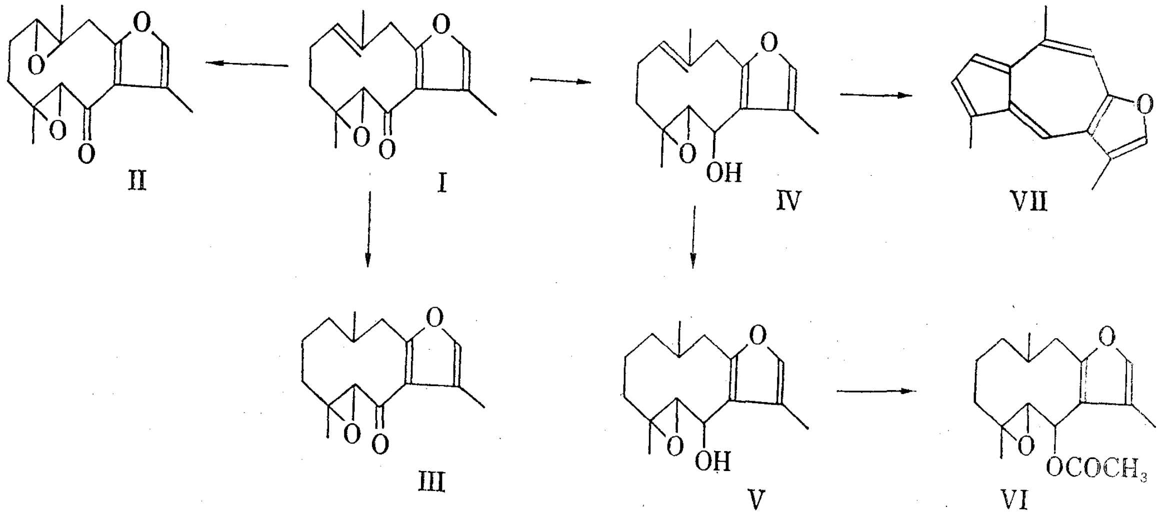

Chart 2

On the basis of the above evidence, formula I is proposed as the structure of zederone.

With the structure of zederone derived, some other spectral properties of zederone may be worthwhile to note.

In order to know whether zederone contained an α- or a β-furyl ketone moiety, the infrared spectra of furyl ketones were investigated at the early stage of the present work. It has been reported that β-furyl ketones show two maxima at 1570—1560 and 1520—1500 cm^{-1} which are attributed to C=C stretching vibration, a strong absorption at 1155—1150 cm^{-1} with an intensity next to that of the C=O stretching frequencies, and a characteristic sharp band at 875—870 cm^{-1}.[11,12] While in α-furyl ketones a single band occurring between 1590 and 1560 cm^{-1} is the only significant feature in the C=C stretching vibration region, no strong band near 1160 cm^{-1} is found and the band around 880 cm^{-1} is observed as broadened or split into two or three.[12] The infrared spectrum of zederone shows merely a single bands at

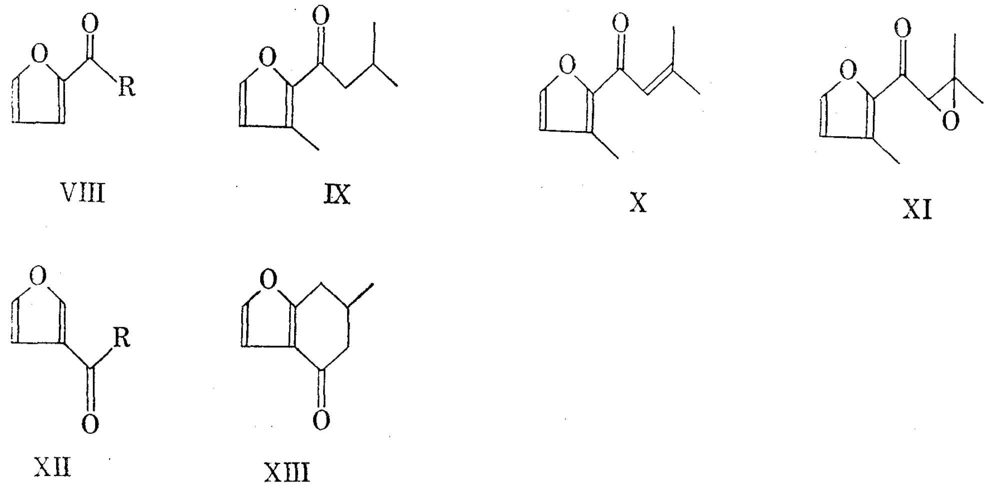

Chart 3

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[11] A. Fujino and M. Yamaguchi, "Sekigaisen Kyushu Supekutoru," Vol. 3, Nankodo Co., Ltd., Tokyo. 1958, p. 101.

[12] M. Yamaguchi, *Bunseki Kagaku*, 7, 210 (1958).

1524 cm^{-1} in the region 1600—1500 cm^{-1}, no strong band nearby 1160 cm^{-1}, and two bands at 898 and 882 cm^{-1} whose intensities are both weak. These spectral properties seem to indicate that zederone belongs to α-furoyl derivatives. However, accepting the formulating I for zederone, it thus appears that the infrared spectral characters deduced from furyl ketones in unstrained systems cannot be applicable to those of furyl ketones with strained features as is indeed the case.

Further, attention was directed to the ultraviolet spectra of furyl ketones. They must provide some evidence about the mode of conjugation. α-Furyl ketones (VIII) exhibit a maximum at 275 mμ.[13] The band in elscholzia ketone (IX) is essentially unchanged, appearing at 275 mμ, a fact which demonstrates that the alkyl substitution at the β-position of furan ring has no effect on the absorption. The bathochromic shift is observed in naginata ketone (X) which has a chromophore where an α-furoyl system is further conjugated with an ethylenic bond, showing the maximum at 295 mμ.[14] Furthermore, naginata ketone epoxide (XI), having an epoxide ring conjugated with an α-furyl ketone grouping, exhibits its absorption band at 282 mμ located midway between those of the above two chromphores. On the other hand, β-furyl ketones (XII) absorb in the 250—255 mμ region.[15] The absorption of evodone (XIII) occurs at 266 mμ[16] indicating that the fusion of a ring with the furan nucleus gives rise to the bathochromic shift by 11—16 mμ. No analogy is available in β-furoyl systems whose carbonyl groups are further cross-conjugated with ethylenic linkages or epoxy-rings. In a β-furyl ketone system, however, further cross-conjugation with an ethylenic bond or an epoxide function is anticipated to cause a considerable bathochromic shift of the maximum as compared with an unstrained system. The observed absorption maximum of zederone at 284 mμ also implies it to be a member of an α-furyl ketones. However, bearing in mind the derived structure I for zederone, it is concluded that the observed bathochromic displacement in the ultraviolet absorption of zederone, a β-furyl ketone, must account for the strained and consequently distorted feature of the molecule.

Experimental[17]

Isolation of Zederone——The crude drug "Ga-jutsu," the dried rhizomes of *Curcuma zedoaria* Roscoe, was extracted with MeOH. The light petroleum soluble fraction of the extract was steam-distilled. The residue was chromatographed over alumina. Benzene eluate gave a crystalline substance which was crystallized from AcOEt to yield zederone (I) as colorless needles, mp 153.5—154°, $[\alpha]_D$ +265.8° (c=5.0), mol. wt. 246 (mass spec.), *Anal.* Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.11; H, 7.33, UV λ_{max}^{EtOH} mμ (log ε): 213 (4.07), 232 (3.82), 284 (3.52). IR (KBr) cm^{-1}: 1661 (conjugated ketone). NMR (100Mcps, $CDCl_3$): doublet (3H) at 1.33 (J=0.8, $-\mathrm{CH}\underset{\mathrm{O}}{\underset{\diagdown\diagup}{-}}\mathrm{C(C\underline{H}_3)-CH_2}-$), singlet (3H) at 1.60 ($\mathrm{(C\underline{H}_3)-C{=}C\langle}$), doublet (3H) at 2.10 (J=1.3, β-$\mathrm{C\underline{H}_3}$- of furan), AB quadruplet (2H) at 3.69, 3.72 (J=16.5, $\rangle\mathrm{C-C\underline{H}_2}$-furan), singlet (1H) at 3.78 ($-\mathrm{CO}\underset{\mathrm{O}}{\underset{\diagdown\diagup}{-}}\mathrm{C\underline{H}-C\langle}$), quadruplet (1H) at 5.47 (J_1=10.9, J_2=4.3, $\mathrm{-CH_2C\underline{H}{=}C\langle}$), quadruplet (1H) at 7.07 (J=1.3, α-$\underline{\mathrm{H}}$- of furan), NMR (100 Mcps, C_6H_6): doublet and singlet (6H) at 1.22 ($-\mathrm{CH}\underset{\mathrm{O}}{\underset{\diagdown\diagup}{-}}\mathrm{C(C\underline{H}_3)-CH_2}-$ and $\mathrm{C\underline{H}_3-C{=}C\langle}$), doublet (3H) at 2.14 (J=1.3, β-$\mathrm{C\underline{H}_3}$- of furan), AB quadruplet (2H) at 3.28, 3.39 (J=16.7, $\geqslant\mathrm{C-C\underline{H}_2}$-furan), singlet (1H) at 3.43 ($-\mathrm{CO-C\underline{H}}\underset{\mathrm{O}}{\underset{\diagdown\diagup}{-}}\mathrm{C\langle}$), quadruplet (1H) at 4.90 (J_1=11, J_2=4, $\mathrm{-CH_2-C\underline{H}{=}C\langle}$). Vanillin-HCl reaction: + (scarlet), pine wood test: + (violet), Ehrlich reaction: + (red), Liebermann-Burchard reaction: + (purple).

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13) R.F. Raffauf, *J. Am. Chem. Soc.*, **72**, 753 (1950); P. Grammaticakis, *Bull. Soc. Chim. France*, **1953**, **866**.

14) T. Ueda, *Nippon Kagaku Zasshi*, **81**, 1751 (1960).

15) T. Matsuura, K. Naya, N. Ichikawa, and T. Kubota, *Bull. Chem. Soc. Japan*, **35**, 1695 (1962).

16) H. Stetter and R. Lauterbach, *Ber.*, **93**, 603 (1960).

17) Melting points are uncorrected. Optical rotations were measured in $CHCl_3$ solution. NMR spectra were determined at 60 Mcps unless specified to the contrary. Chemical shifts are given in ppm from internal Me_4Si and coupling constants (J) in cps. Signals are expressed without fine splittings.

Oxidation of Zederone with Perbenzoic Acid——Zederone (38 mg) in $CHCl_3$ (0.5 ml) was treated with BzO_2H (30 mg) at 0° for 37 hr. Upon isolation, the product (43 mg) was chromatographed over alumina (2 g). Elution with benzene and crystallization from AcOEt gave zederone epoxide (II) as colorless needles, mp 147—148°, $[\alpha]_D$ +157.1° (c=2.9). *Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.46; H, 6.84, UV λ_{max}^{EtOH} mμ (log ε): 232 (3.90), 284 (3.58). IR (KBr) cm^{-1}: 1667 (conjugated ketone), NMR ($CDCl_3$): singlet (3H) at 1.15 ($C\underline{H}_3\text{-}\underset{\diagdown O \diagup}{C\text{—}CH}\text{-}$), singlet (3H) at 1.33 ($C\underline{H}_3\text{-}\underset{\diagdown O \diagup}{C\text{—}CH}\text{-}$), doublet (3H) at 2.19 (J=1.2, $\beta\text{-}C\underline{H}_3\text{-}$ of furan), AB quadruplet (2H) at 2.81, 3.71 (J=16.9, $\text{-}\underset{\diagdown O \diagup}{CH\text{-}C}\text{-}C\underline{H}_2\text{-}$furan), singlet (1H) at 3.78 ($\text{-}CO\text{-}\underset{\diagdown O \diagup}{C\underline{H}\text{-}C}\langle$), quadruplet (1H) at 7.09 (J=1.2, $\alpha\text{-}\underline{H}\text{-}$ of furan).

Partial Hydrogenation of Zederone over Platinum Oxide in Methanol——Zederone (210 mg) was hydrogenated using PtO_2 (0.1 g) in MeOH (10 ml). After consumption of 1 mole of H_2, the mixture was worked up as usual and distillation under reduced pressure gave a mixture of the dihydro-derivatives (III) as a colorless oil, $[\alpha]_D$ +108.0° (c=8.0). *Anal.* Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.51; H, 8.10. UV λ_{max}^{EtOH} mμ (log ε): 214 (3.94), 279 (3.44), IR (liquid) cm^{-1}: 1674 (conjugated ketone), NMR ($CDCl_3$): two doublets (3H) at 1.14, 1.18 (J=6, $C\underline{H}_3\text{-}CH\langle$), two singlets (3H) at 1.32, 1.37 ($C\underline{H}_3\text{-}\underset{\diagdown O \diagup}{C\text{—}C}\langle$), two doublets (3H) at 2.14, 2.22 (J=1.2, $\beta\text{-}C\underline{H}_3\text{-}$ of furan), two singlets (1H) at 3.96, 4.19 ($\text{-}CO\text{-}\underset{\diagdown O \diagup}{C\underline{H}\text{—}C}\langle$), two quadruplets (1H) at 7.02, 7.07 (J=1.2, $\alpha\text{-}\underline{H}\text{-}$ of furan).

Reduction of Zederone with Lithium Aluminum Hydride——Zederone (200 mg) in ether (10 ml) was stirred with $LiAlH_4$ (0.1 g) at 0° for 30 min. Upon isolation in the usual way, the product (202 mg) was crystallized from light petroleum to give the alcohol (IV) as colorless needles, mp 132—133°, $[\alpha]_D$ +153.7° (c=3.8). *Anal.* Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.71; H, 8.19. UV λ_{max}^{EtOH} mμ (log ε): 224 (3.91). IR (KBr) cm^{-1}: 3448 (hydroxyl), NMR ($CDCl_3$): singlet (3H) at 1.62 ($C\underline{H}_3\text{-}\underset{\diagdown O \diagup}{C\text{—}C}\langle$), broad singlet (3H) at 1.74 ($C\underline{H}_3\text{-}C{=}C\langle$), doublet (3H) at 2.01 (J=1.3, $\beta\text{-}C\underline{H}_3\text{-}$ of furan), broad peak (1H) at 2.94 ($\text{-}CH(OH)\text{-}\underset{\diagdown O \diagup}{C\underline{H}\text{-}C}\langle$), broad singlet (2H) at 3.48 ($\rangle C{=}C\text{-}C\underline{H}_2\text{-}$furan), broad peak (2H) at 5.21 ($\text{-}C\underline{H}(OH)\text{-}\underset{\diagdown O \diagup}{CH\text{—}C}\langle$, $\text{-}CH_2\text{-}C\underline{H}{=}C\langle$), quadruplet (1H) at 7.05 (J=1.3, $\alpha\text{-}\underline{H}\text{-}$ of furan).

Oxidation of the Alcohol with Manganese Dioxide——The alcohol (IV) (53 mg) in $CHCl_3$ (10 ml) was stirred overnight at room temperature with MnO_2 (0.5 g). The solids are filtered off and the filtrate was evaporated to give the product (51 mg) which on crystallization from AcOEt afforded zederone (I) as colorless needles, mp 151—153°, identified by mixed mp and by comparison of IR and NMR spectra.

Partial Hydrogenation of the Alcohol over Platinum Oxide in Methanol——The alcohol (IV) (1.23 g) was hydrogenated with PtO_2 (0.15 g) in MeOH (40 ml). Isolation in the customary manner and crystallization from light petroleum yielded the dihydro-alcohol (V) as colorless needles (0.55 g), mp 106—107°, $[\alpha]_D$ +106.8° (c=7.9). *Anal.* Calcd. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.14; H, 8.84. IR (KBr) cm^{-1}: 3413 (hydroxyl). NMR ($CDCl_3$): doublet (3H) at 1.01 (J=6.5, $C\underline{H}_3\text{-}CH\langle$), singlet (3H) at 1.89 ($C\underline{H}_3\text{-}\underset{\diagdown O \diagup}{C\text{—}C}\langle$), doublet (3H) at 2.06 (J=1.3, $\beta\text{-}C\underline{H}_3\text{-}$ of furan), doublet (1H) at 3.31 (J=2.2, $\text{-}CH(OH)\text{-}\underset{\diagdown O \diagup}{C\underline{H}\text{—}C}\langle$), doublet (1H) at 5.04 (J=2.2, furan-$C\underline{H}(OH)\text{-}\underset{\diagdown O \diagup}{CH\text{—}C}\text{-}$), quadruplet (1H) at 7.03 (J=1.3, $\alpha\text{-}\underline{H}\text{-}$ of furan).

Acetylation of the Dihydro-alcohol——The dihydro-alcohol (V) (30 mg) in pyridine (0.5 ml) was treated overnight at room temperature with excess of AcCl. After isolation, the product was crystallized from AcOEt to give the dihydro-alcohol acetate (VI) as colorless needles, mp 120—121°, $[\alpha]_D$ +153.0° (c=8.4). *Anal.* Calcd. for $C_{17}H_{24}O_4$: C, 69.87; H, 8.27. Found: C, 70.17; H, 8.43. IR (KBr) cm^{-1}: 1730, 1213 (acetoxyl). NMR (CCl_4): doublet (3H) at 1.04 (J=6.3, $C\underline{H}_3\text{-}CH\langle$), singlet (3H) at 1.77 ($C\underline{H}_3\text{-}\underset{\diagdown O \diagup}{C\text{-}C}\langle$), doublet (3H) at 2.04 (J=1.0, $\beta\text{-}C\underline{H}_3\text{-}$ of furan), singlet (3H) at 2.06 ($C\underline{H}_3\text{-}CO\text{-}O\text{-}$), doublet (1H) at 3.22 (J=1.9, $\text{-}CH(OCOCH_3)\text{-}\underset{\diagdown O \diagup}{C\underline{H}\text{—}C}\langle$), doublet (1H) at 6.47 (J=1.9, furan-$C\underline{H}(OCOCH_3)\text{-}\underset{\diagdown O \diagup}{CH\text{—}C}\langle$), quadruplet (1H) at 7.16 (J=1.0, $\alpha\text{-}\underline{H}\text{-}$ of furan).

Dehydrogenation of the Alcohol with Palladium-carbon——The alcohol (IV) (1.4 g) was heated with 10% Pd-C (1.0 g) under N_2 at 320—325° for 10 min. The mixture was dissolved in light petroleum and the catalyst was removed by filtration. The filtrate was adsorbed on silica gel (40 g) and eluted with light petroleum to yield linderazulene (VII) as a violet oil (50 mg) which was dissolved in EtOH and treated with 1,3,5-trinitrobenzene. The resulting crystals on crystallization from EtOH afforded the complex as maroon needles, mp 153—153.5°. *Anal.* Calcd. for $C_{21}H_{17}O_7N_3$: N, 9.93. Found: N, 9.65, UV λ_{max}^{EtOH} mμ (log ε): 225 (4.25), 278 (4.35), 288 (4.40), 296 (4.39), 315 (4.01), 350 (3.44), 358 (3.51), 367 (3.56), 374 (3.47), 387 (3.39), identified by mixed mp and by comparison of TLC and UV spectra.

Oxidation of Naginata Ketone with Hydrogen Peroxide——To naginata ketone (X) (109 mg) in MeOH (5 ml) was added 30% H_2O_2 (0.4 ml) in 4N NaOH solution (0.4 ml) and the mixture was set aside at 0° for 3 days. After isolation in the usual way, the product (75 mg) was crystallized from light petroleum to furnish naginata ketone epoxide (XI) as colorless needles, mp 76—77°, *Anal.* Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.57; H, 6.68. UV λ_{max}^{EtOH} mμ (log ε): 281 (4.18). IR (KBr) cm^{-1}: 1670 (conjugated ketone), NMR (CCl_4): two singlets (3H each) at 1.25, 1.48 ($((C\underline{H}_3)_2C\underset{\diagdown O \diagup}{—}CH–)$), singlet (3H) at 2.39 (β–$C\underline{H}_3$– of furan), singlet (1H) at 3.89 ($–C\underset{\diagdown O \diagup}{—}C\underline{H}–CO–$), doublet (1H) at 6.41 ($J=1.6$, β'–$\underline{H}$– of furan), doublet (1H) at 7.45 ($J=1.6$, α'–$\underline{H}$– of furan).

Acknowledgement We are indebted to Dr. T. Ueda, Government Industrial Research Institute, Osaka, for naginata ketone, and to Dr. H. Minato, Research Laboratory, Shionogi & Co., Ltd., for linderazulene. Thanks are also due to Dr. M.C. Woods, Varian Associates, and Research Laboratories, Takeda Chemical Industries, Ltd., for the NMR spectra, to Naka works, Hitachi Ltd., for the mass spectrum, and to Analytical Laboratories, this Institute, for microanalyses and the IR and NMR spectra.