Diterpenoids of *Roylea calycina* (Roxb.) Briq.

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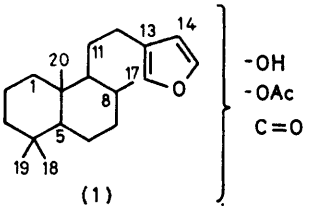
The structures of three new diterpenes, calyone, calyenone, and precalyone, isolated from the aerial portion of *Roylea calycina* have been shown to be 3-acetoxy-15,16-epoxy-9-hydroxylabda-13(16),14-dien-7-one (2), 3-acetoxy-15,16-epoxylabda-8,13(16),14-trien-7-one (5), and 3-acetoxy-9,13;15,16-diepoxylabda-14-en-7-one (7), respectively, by chemical and spectroscopic studies. Precalyone showed antitumor activity against P-388 lymphocytic leukaemia.

ROYLEA CALYCINA (Roxb.) Briq. (Labiatae), a shrub growing to a height of 0.9—1.5 m is cultivated in India as a hedge plant. During a programme for screening Indian plants at this Institute (C.D.R.I.), an extract of the leaves and stems of *R. calycina* in 50% aqueous ethanol showed significant activity against P-388 lymphocytic leukaemia (PS) in mice.[1] Follow-up studies concentrated this activity in the water-insoluble fraction. Repeated column chromatography of this material over silica gel furnished calyenone (0.01%), epicalyone (0.002%), and calyone (0.04%). Since calyone was obtained in the largest yield it was investigated in detail.

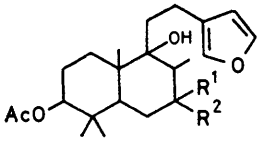
The u.v. and i.r. spectra [$\lambda_{max.}$ 213 nm (ε 4 677) and $\nu_{max.}$ 1 502, 872, and 785 cm^{-1}] of calyone, $C_{22}H_{32}O_5$ (M^+ 376), indicated the presence of a furan ring. That the furan ring is β-substituted was deduced from its ^1H n.m.r. spectrum which showed signals at δ 7.36 and 7.25 for two α-protons and 6.30 for one β-proton. The i.r. spectrum also showed the presence of an ester function (1 740 cm^{-1}), a saturated carbonyl group (1 715 cm^{-1}), and a hydroxy-group (3 415 cm^{-1}). The ester was shown to be an acetate [δ 2.07 (3 H, s)] by the ^1H n.m.r. spectrum, which also showed the hydroxy-proton as a concentration-dependent signal around δ 2.25, exchangeable with D_2O. Other features of the ^1H n.m.r. spectrum were the presence of three tertiary methyl singlets at δ 0.85, 1.00, and 1.23, a doublet for a secondary methyl at δ 1.15 (J 6.5 Hz), in addition to the twelve saturated methylene and methine proton signals which appeared as a multiplet in the region δ 1.60—2.90. These data indicated that the compound was a furano-diterpenoid for which the skeleton (1) was assigned by analogy with other known compounds.

The resistance to acetylation and the absence of a signal due to C*H*OH in the ^1H n.m.r. spectrum of calyone indicated the tertiary nature of the hydroxy-group. Of the three possible positions for this function, at C-5, -8, and -9, C-8 was ruled out in view of the appearance of the C-8-methyl signal as a doublet. The ready dehydration of calyone with methanol–ammonia yielding an αβ-unsaturated ketone ($\lambda_{max.}$ 251 nm) located the carbonyl function β to the tertiary hydroxy-group, *viz.*, at C-7. The appearance of the C-8-methyl signal as a singlet at δ 1.85 in the dehydrated compound, later identified as calyenone, fixed the hydroxy-group in calyone at C-9.

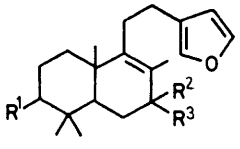
Position C-3 for the acetoxy-group was considered on biogenetic grounds;[2] this was supported by the appearance of the C-3 methine proton in the n.m.r. spectrum as a triplet at δ 4.75, which on deacetylation shifted to δ 3.52. This assignment was confirmed by the fact that in the ^{13}C n.m.r. spectrum, the C-3 signal appeared at δ 77.31 in calyone and at δ 76.79 in calyenone; if the acetoxy-function were at C-1, a deshielding of 4.5 p.p.m. could be expected on dehydration.[3] Thus structure (2) can be assigned for calyone.



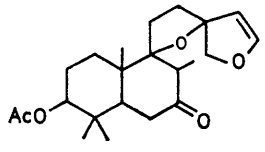
(1)



(2) R^1R^2 = O
(3) R^1 = OH, R^2 = H



(4) R^1 = OH, R^2R^3 = O
(5) R^1 = OAc, R^2R^3 = O
(6) R^1 = R^2 = OH, R^3 = H



(7)

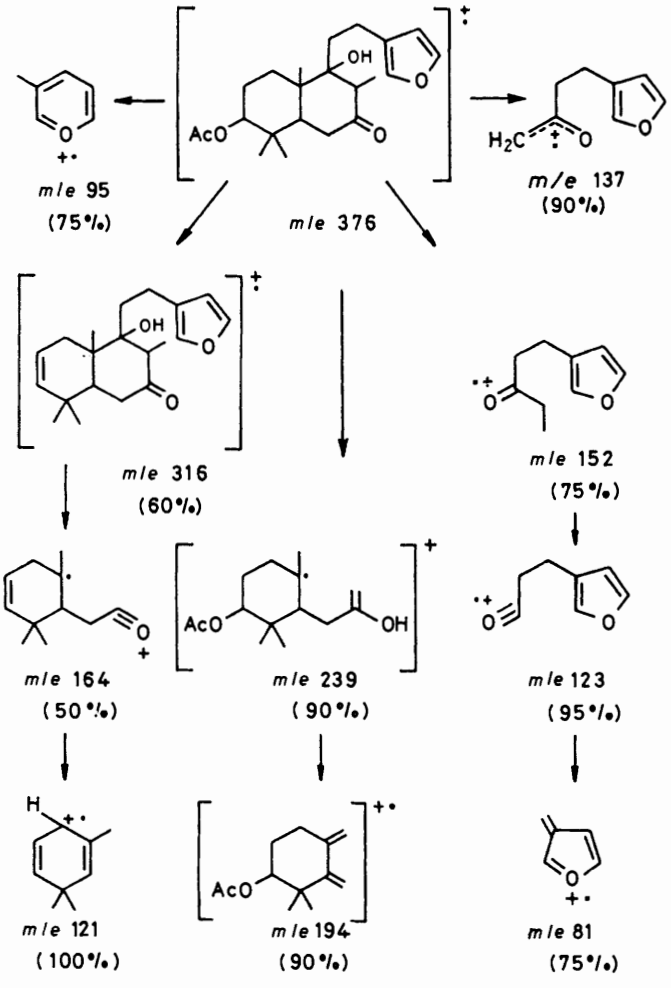
The mass spectrum of calyone is consistent with the proposed structure (Scheme). Of particular interest is the appearance of two very intense peaks at *m/e* 239 and 137; this is explained by assuming a homolytic cleavage of the C-9–C-10 bond, followed by a 1,2-shift of the C-8 methyl and transfer of the hydroxy-proton to C-8. A McLafferty rearrangement would now lead to the two ions mentioned above.

As mentioned earlier, attempted deacetylation of calyone with methanol–ammonia resulted in dehydr-

ation. Treatment with 2% ethanolic sodium hydroxide yielded (4) by simultaneous dehydration and deacetylation, while reduction with sodium borohydride furnished the hydroxy-acetate (3).

Calyenone, $C_{22}H_{30}O_4$ (M^+ 358), was also found to be a furano-diterpene acetate from its mass and ^1H n.m.r. spectral data. The absorption spectra [$\lambda_{max.}$ 217 (ε 11 870) and 251 nm (12 460), and $\nu_{max.}$ 1 502, 872, 785, and 1 665 cm^{-1}] showed the presence of furan and αβ-unsaturated ketone moieties in addition to an acetate function (1 725 cm^{-1}). The ^1H n.m.r. spectrum of calyenone was similar to that of calyone but, instead of signals for the secondary methyl and the hydroxy-protons, it showed a singlet at δ 1.85 (3 H) indicating the presence of a methyl group on a double bond. Reduction with lithium aluminium hydride caused the reduction of carbonyl group as well as deacetylation to furnish (6). Structure (5), assigned to calyenone on the basis of these data, was confirmed by its comparison with the product obtained by dehydration of calyone.

Epicalyone, $C_{22}H_{32}O_5$ (M^+ 376), whose spectral properties (see Experimental section) are very close to those of calyone, is considered to be an epimer of the latter; detailed study could not be undertaken as the compound was obtained in very small yield.



SCHEME

None of the compounds described above showed any antitumor activity and, since these compounds were obtained by chromatography on silica gel, a modified method of extraction was used which resulted in the isolation of a new diterpenoid, now designated as precalyone. The i.r. spectrum of precalyone, $C_{22}H_{32}O_5$ (M^+ 376), did not show any bands at 3 650—3 200 or at 1 500, 872, and 785 cm^{-1}, attributable to the hydroxy and β-substituted furan function, respectively, as observed in (2), (5), and epicalyone. The absorption bands at 1 730 and 1 715 cm^{-1}, however, indicated the presence of acetoxy and carbonyl groups.

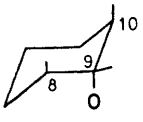
The ^1H n.m.r. spectrum of precalyone had certain features in common with that of calyone. The main difference was that the characteristic signals for furan protons were absent. Instead, two AB quartets, one at δ 5.13 and 6.45 (2 H, J 3.0 Hz) and the other at δ 4.09 and 4.48 (2 H, J 10.0 Hz) were observed. The former was probably due to the presence of an enol ether system and the latter to a CH_2O group. This suggested the presence of a spiro-union. The three tertiary methyl singlets appeared at δ 0.72, 0.96, and 1.19 and the secondary methyl protons at δ 1.04 (d, J 6.5 Hz). The singlet at δ 2.00 was assigned to the acetoxy-function and the multiplet at δ 4.76 to the proton adjacent to it (C*H*OAc). The remaining methylene and methine protons showed absorptions between δ 1.83 and 2.70. The data was suggestive of structure (7) for precalyone; this was confirmed by the ready conversion of precalyone to calyone by mildly acidic reagents (*e.g.* silica gel).

In the ^{13}C n.m.r. spectra of (2), (5), and (7) the furanone carbons could easily be recognised in the low-field region. C-13 appeared as the only singlet in SFORD spectra while C-14 resonated at higher field than C-15 and C-16. Further, in structures (2) and (5) the C-16 resonance was distinguished from that of C-15 because of slight shielding due to substitution at C-13 whilst in the case of (7) the C-16 resonance appeared as a triplet at δ 80.84. In (2) and (7) the chemical shifts appropriate to C-5 and C-8 were delineated by considering the shielding effect of the hydroxy-group at C-9 which resulted in upfield shift for C-5 in (2) relative to the same carbon atom in (7), whereas in (5) C-5 appeared as a doublet at δ 44.53 and C-8 as a singlet at δ 166.11. Thus after assignment of all the doublets had been made, the remaining one around δ 77.30 was ascribed to C-3 in the spectrum of each compound. In the SFORD spectrum of (2), (5), and (7), differentiation between the two singlets appropriate to C-4 and C-10 was achieved by noting the larger number of deshielding β-effects which resulted in a down-field shift for C-10. Of the two low-field singlets, the one at the lower field was assigned to the C-7 carbonyl carbon in each compound. In the ^{13}C n.m.r. spectrum of (5) the assignment of the low-field singlet at δ 130.60 to C-9 was straightforward.[4] Similarly, in (2) the remaining

singlet at δ 81.49 was ascribed to C-9. In (7) differentiation between two mid-field singlets at δ 95.98 and 94.05 for C-9 and -13 was difficult. However, on the basis of literature values [4] and because of a larger number of β-substituents, the lower-field signal at δ 95.98 was assigned to C-9. Of the three high-field triplets for C-2, -11, and -12 in the spectrum of each compound, the one at higher field (δ 22.77) was assigned to C-2 because it had fewest β-substituents and was shifted upfield due to the γ-effect of *axial* substituents at C-4 as well as at C-10. The differentiation of peaks for C-11 and C-12 was based on the γ-effect of C-17 and C-20 methyl groups. It is expected that due to a γ-effect the chemical shift of C-11 should be upfield to that of C-12. The triplets associated with C-1 of (2) and (7) were similar but in the case of (5) the chemical shift of this carbon was δ 4.0 upfield due to conformational changes in ring B.

Of the C-17, -18, -19, and -20 methyl resonances, the signal which appeared at lowest field was ascribed as *equatorial* and that at highest field to C-20, which is influenced by three 1,3-*diaxial* hydrogen interactions. The signals for C-17 and -19 were distinguished by considering the larger number of deshielding effects for the C-19 methyl group. The quartet at δ 21.13 was assigned to the acetoxy-methyl group in each compound.

Solvent-induced Shift.—In the ^{1}H n.m.r. spectrum of (2) in C_6D_6 the C-17 methyl signal at δ 1.15 (d, *J* 6.5 Hz) was shifted upfield by δ 0.15 relative to its position when $CDCl_3$ was used as solvent whereas in (5) and (7) the C-17 methyl signals showed upfield shifts of δ 0.27 and 0.12, respectively. Thus these results agreed with the formation of a collision complex in which the anisotropy of the benzene ring was such that an *axial* methyl group would be expected to be shielded whilst *equatorial* protons would be affected much less and perhaps even deshielded slightly. From these facts an *axial* configuration could be assigned to the C-17 methyl group in (2), (5), and (7). The signal of the methyl or acetoxy group of (2), (5), and (7) moved upfield by δ 0.33, 0.33, and 0.48, respectively, in C_6D_6 in comparison to $CDCl_3$. These results suggested that the geometry of the benzene–carbonyl collision complex was such as to shield the protons of the methyl function adjacent to the keto-group.[5] The upfield shift of δ 0.15 and 0.57 of the signals due to methyl groups at C-8 and -10, respectively, on replacing $CDCl_3$ by C_6D_6, indicated the relative configur-



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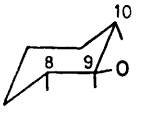

(9)

ation (8) or (9) for ring B in these compounds. Structure (8), which permits a *trans* junction of ring A and B in (2), (5), and (7), appeared to be more likely than structure (9); this is in agreement with the observation that in the ^{13}C n.m.r. spectra of calyone and calyenone, the C-5 methine absorptions appeared at δ 40.98 and 44.53, respectively. The upfield shift of 3.55 p.p.m. in (5) confirmed the *axial* nature of the hydroxy-substituent.[3] Thus the C-8 methyl and C-9 hydroxy-functions in calyenone have a *trans* relationship.

Biological Activity.—The various fractions of *R. calycina* were tested for their anticancer activity at the Cancer Chemotherapy National Service Centre of the National Institute of Health, Bethesda, U.S.A., according to the CCNSC protocols,[6] in P-388 lymphocytic leukaemia of mice (PS system). While precalyone showed T/C 143 at 50 mg kg^{-1}, the other diterpenoids were found to be inactive.

EXPERIMENTAL

U.v. spectra were recorded on a Perkin-Elmer 202 spectrophotometer and i.r. spectra on Perkin-Elmer 137 Infracord or 177 grating instruments. ^{1}H N.m.r. spectra were recorded on a Varian A-60D spectrometer and ^{13}C n.m.r. spectra on a JEOL FX-100 Fourier-transform spectrometer operating at 25.05 MHz with a spectral width of 6 024 Hz. All n.m.r. spectra were run on solutions in $CDCl_3$ unless stated otherwise. Chemical shifts are expressed relative to internal tetramethylsilane. Mass spectra were determined on a Hitachi RMU-6E mass spectrometer fitted with a direct inlet system. Optical rotations were measured for solutions in $CHCl_3$ on a JASCO DIP-180 automatic polarimeter.

Isolation of Constituents.—The air-dried powdered leaves and stems of *R. calycina* (28 kg) were extracted with 95% ethanol (4 × 45 l) by cold percolation and the extract was concentrated under reduced pressure (below 50 °C). Dilution with water, filtration, and drying yielded a solid (1.8 kg). Part of this material (30.0 g) was chromatographed over silica gel (900 g). Graded elution was effected with benzene followed by benzene–ethyl acetate mixtures. A total of 110 fractions of 50 ml each were collected and mixed on the basis of t.l.c. and ^{1}H n.m.r. data.

Calyenone (2).—Fractions 36—48 were mixed (0.40 g) and rechromatographed over silica gel (20 g). Elution was effected with benzene followed by solvents of increasing polarity. Fractions 8—21 were combined and crystallized from methanol–light petroleum to afford 3-*acetoxy*-15,16-*epoxylabda*-8,13(16),14-*trien*-7-*one* (5) as needles, m.p. 102°, $[\alpha]_D^{25}$ −24.2° (*c* 1.96); $\lambda_{max.}$ (EtOH) 217 (ε 11 870) and 251 nm (12 460); $\nu_{max.}$ (KBr) 1 725, 1 665, 1 502, 872, and 785 cm^{-1}; δ 7.37 (1 H, m), 7.30 (1 H, m), 6.30 (1 H, m), 4.70 (1 H, m), 3.00—1.20 (11 H, m), 2.07 (3 H, s), 1.85 (3 H, s), and 1.15, 1.02, and 0.90 (9 H, 3 s); δ_C: 199.28 (s, C-7), 170.22 (s, CH_3CO_2), 166.11 (s, C-8), 142.98 (d, C-15), 138.61 (d, C-16), 130.60 (s, C-9), 124.34 (s, C-13), 110.54 (d, C-14), 76.79 (d, C-3), 44.53 (d, C-5), 40.45 (s, C-10), 36.57 (s, C-4), 34.52 (t, C-1), 30.14 (t, C-6), 29.41 (t, C-11), 26.97 (q, C-18), 24.27 (t, C-12), 22.86 (t, C-2), 21.34 (q, C-19), 21.13 (q, CH_3CO_2), 18.05 (q, C-17), and 11.47 (q, C-20); *m/e* 358 (M^+), 343 (M − 15), 298 (M − 60), 203 (base peak), 95, and 81 (Found: C, 73.8; H, 8.65. $C_{22}H_{30}O_4$ requires C, 73.71; H, 8.44%).

Reduction of Calyenone with Lithium Aluminium Hydride.—To a stirred suspension of lithium aluminium hydride (LAH) (25 mg) in sodium-dried THF (4 ml) a solution of calyenone (2) (60 mg) in dry THF (5 ml) was added and the stirring was continued for 2 h. The excess

of LAH was decomposed with EtOAc (2 ml) followed by H_2O (5 ml). The resulting mixture was filtered, the residue washed with EtOAc (10 ml), and the filtrate re-extracted with EtOAc (4 × 20 ml). The combined organic layers were washed with H_2O, dried (Na_2SO_4), and concentrated, and the residue was purified by p.l.c. to furnish 15,16-*epoxylabda*-8,13(16),14-*triene*-3,7-*diol* (6) (25 mg) as the major product, $[\alpha]_D^{25}$ −60° (*c* 1.0); $\lambda_{max.}$ (EtOH) 217 nm; $\nu_{max.}$ (neat) 3 500, 1 500, 880, and 785 cm^{-1}; δ 7.32 (1 H, m), 7.21 (1 H, m), 6.26 (1 H, m), 4.09 (1 H, m), 2.43 (1 H, m), 2.60—1.20 (13 H, m), 1.70 (3 H, s), and 1.05, 0.97, and 0.88 (9 H, 3 s, 3 × CH_3); *m/e* 318 (M^+), 300, 267, 236, 133, 121 (base peak), 95, and 81 (Found: C, 75.3; H, 9.45. $C_{20}H_{30}O_3$ requires C, 75.43; H, 9.50%).

Epicalyone.—T.l.c. and ^1H n.m.r. of fractions 26—31 indicated them to belong to the same diterpenoid compound. These fractions were, therefore, combined and concentrated to afford epicalyone (0.01 g), $[\alpha]_D^{25}$ −58.70° (*c* 0.13); $\lambda_{max.}$ (EtOH) 213 nm (ε 5 100); $\nu_{max.}$ (neat) 3 420, 1 740, 1 504, 875, and 778 cm^{-1}; δ 7.35 (1 H, m), 7.25 (1 H, m), 6.28 (1 H, m), 4.74 (1 H, m), 3.00—1.15 (13 H, m), 2.08 (3 H, s), 1.10 (3 H, s), 1.02 (3 H, d, *J* 6.5 Hz), and 0.95 and 0.85 (6 H, 2s); *m/e* 376 (M^+), 361, 316, 301, 239, 194, 152, 137, 121 (base peak), 95, and 81 (Found: C, 70.25; H, 8.4. $C_{22}H_{32}O_5$ requires C, 70.19; H, 8.57%).

Calyone (2).—Fractions 57—70 were combined to afford (2) which was crystallized twice from methanol–light petroleum to furnish 3-*acetoxy*-15,16-*epoxy*-9-*hydroxylabda*-13(16),14-*dien*-7-*one* (2) (0.20 g) as needles, m.p. 142°, $[\alpha]_D^{25}$ −45.7° (*c* 2.1); $\lambda_{max.}$ (EtOH) 213 nm (ε 4 677); $\nu_{max.}$ (KBr) 3 415, 1 740, 1 715, 1 502, 872, and 785 cm^{-1}; δ 7.36 (1 H, m), 7.25 (1 H, m), 6.30 (1 H, m), 4.75 (1 H, t, *J* 2.0 Hz), 2.90—1.60 (13 H, m), 2.00 (3 H, s), 1.23 (3 H, s), 1.15 (3 H, d, *J* 6.5 Hz), and 1.00 and 0.25 (6 H, 2s); δ_C 211.18, (s, C-7), 170.49 (s, CH_3CO_2), 142.95 (d, C-15), 138.49 (d, C-16), 124.81 (s, C-13), 110.66 (d, C-14), 81.49 (s, C-9), 77.31 (d, C-3), 50.96 (d, C-8), 43.03 (s, C-10), 40.98 (d, C-5), 38.51 (t, C-1), 37.04 (s, C-4), 34.93 (t, C-6), 27.65 (q, C-18), 25.71 (t, C-11), 22.77 (t, C-2), 21.60 (t, C-12), 21.48 (q, C-19), 21.13 (q, CH_3CO_2), 16.14 (q, C-17), and 8.27 (q, C-20); *m/e* 376 (M^+), 361, 316, 239, 194, 164, 152, 137, 123, 122, 121 (base peak), 95, and 81 (Found: C, 70.35; H, 8.45. $C_{22}H_{32}O_5$ requires C, 70.19; H, 8.57%).

Dehydration of Calyone.—A solution of calyone (2) (50 mg) in MeOH (5 ml) and NH_4OH (30—32% NH_3; 0.5 ml) was allowed to stand for 48 h. The mixture was concentrated *in vacuo* and the residue was extracted with $CHCl_3$ (2 × 20 ml), washed with H_2O (2 × 15 ml), dried (Na_2SO_4), and concentrated. The product was purified by p.l.c. to furnish the labdatrienone (5) (31 mg) as needles, m.p. 102°.

Alkaline Hydrolysis of Calyone.—A solution of calyone (75 mg) in ethanol (5 ml) and 2% ethanolic NaOH (1.3 ml) was refluxed for 2 h, then cooled, diluted with H_2O (10 ml), and extracted with $CHCl_3$ (4 × 25 ml). The organic layer was washed with H_2O (2 × 10 ml), dried (Na_2SO_4), and concentrated. The product was purified by p.l.c. to furnish 15,16-*epoxy*-3-*hydroxylabda*-8,13(16),14-*trien*-7-*one* (4) (50 mg), $[\alpha]_D^{25}$ −78.29° (*c* 0.47); $\lambda_{max.}$ (EtOH) 210 and 251 nm; $\nu_{max.}$ (neat) 3 450, 1 650, 1 502, 875, and 760 cm^{-1}; δ 7.38 (1 H, m), 7.30 (1 H, m), 6.36 (1 H, m), 3.52 (1 H, m), 2.60—1.20 (12 H, m), 1.83 (3 H, s), and 1.14, 1.03, and 0.90 (9 H, 3 s); *m/e* 316 (M^+), 301 (base peak), 283, 241, 203, 121, 95, and 81 (Found: C, 75.75; H, 8.95. $C_{20}H_{28}O_3$ requires C, 75.90; H, 8.90%).

Reduction of Calyone with Sodium Borohydride.—To a stirred solution of calyone (2) (75 mg) in ethanol (5 ml), $NaBH_4$ (25 mg) was added at room temperature and the stirring continued for 4 h. The mixture was then diluted with H_2O (10 ml) and extracted with $CHCl_3$ (2 × 50 ml). The organic layer was washed with H_2O (2 × 2 ml), dried (Na_2SO_4), and concentrated to afford a residue which was purified by p.l.c. to furnish 3-*acetoxy*-15,16-*epoxylabda*-13(16),14-*diene*-7,9-*diol* (3) (40 mg) as the major product. Crystallization from methanol–light petroleum gave needles, m.p. 113°; $[\alpha]_D^{25}$ −46.48° (*c* 0.36); $\lambda_{max.}$ (EtOH) 217 nm; $\nu_{max.}$ (KBr) 3 450, 1 725, 1 500, 872, and 772 cm^{-1}; δ 7.36 (1 H, m), 7.26 (1 H, m), 6.29 (1 H, m), 4.70 (1 H, m), 3.94 (1 H, m), 2.60—1.50 (14 H, m), 2.10 (3 H, s), 1.21 (3 H, d, *J* 6.5 Hz), and 0.96 and 0.92 (9 H, 2 s); *m/e* 378 (M^+), 318, 300, 236, 181, 163, 123 (base peak), 122, 121, 95, and 81 (Found: C, 69.65; H, 9.2. $C_{22}H_{34}O_5$ requires C, 69.81; H, 9.05%).

Precalyone (7).—The powdered air-dried stems and leaves of *R. calycina* (1.6 kg) were extracted with boiling light petroleum (4 × 4 l) and the filtrate on concentration yielded crystals (20 g) which were recrystallized three times from light petroleum to give 3-*acetoxy*-9,13;15,16-*diepoxylabda*-14-*en*-7-*one* (7) (1.0 g) as needles, m.p. 172—173°; $[\alpha]_D^{25}$ −17.1° (*c* 2.0); $\lambda_{max.}$ (EtOH) 223 nm (ε 9 500); $\nu_{max.}$ (KBr) 1 730 and 1 715 cm^{-1}; δ 6.46 (1 H, d, *J* 3.0 Hz), 5.13 (1 H, d, *J* 3.0 Hz), 4.76 (1 H, m), 4.48 (1 H, d, *J* 10.0 Hz), 4.09 (1 H, d, *J* 10.0 Hz), 2.70—1.83 (12 H, m), 2.00 (3 H, d), 1.19 (3 H, s), 1.04 (3 H, d, *J* 6.5 Hz), and 0.96 and 0.82 (6 H, 2s); δ_C 210.18 (s, C-7), 170.26 (s, CH_3CO_2), 148.27 (d, C-15), 106.99 (d, C-14), 95.98 (s, C-9), 94.05 (s, C-13), 80.84 (t, C-16), 77.46 (d, C-3), 49.96 (d, C-8), 42.53 (s, C-10), 40.15 (d, C-5), 38.22 (2 t, C-1, -6), 36.89 (s, C-4), 29.44 (t, C-11), 27.15 (q, C-18), 26.36 (t, C-12), 22.72 (t, C-2), 21.19 (q, C-19), 21.13 (q, CH_3CO_2), 17.15 (q, C-17), and 9.24 (q, C-20); *m/e* 376 (M^+), 361, 316, 164, 122 (base peak), 121, 95, and 81 (Found: C, 70.5; H, 8.5. $C_{22}H_{32}O_5$ requires C, 70.19; H, 8.51%).

Reaction of Precalyone with IR-120.—A suspension of the diepoxide (7) (75 mg), ethanol (5 ml), and Amberlite IR-120 (H^+ form) (100 mg) was stirred at room temperature for 2 h. The solution was filtered and the solvent removed. The residue was purified by p.l.c. to furnish calyone (2) (55 mg), m.p. 102°, identical with the sample previously isolated (u.v., i.r., n.m.r., and mass spectra).

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