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TRITERPENES OF *LITHOCARPUS* SPECIES

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Key Word Index—*Lithocarpus cornea*; *L. glabra*; *L. hancei*; *L. harlandi*; *L. polystacha*; Fagaceae; triterpenes; 24-methylcycloartanes; chemotaxonomy.

Abstract—The triterpenes of the five *Lithocarpus* species examined comprised members of the friedo- and unrearranged oleanane groups, viz. friedelin, friedelan-3β-ol, taraxerol and β-amyrin. Glutinol was also present, except in *L. harlandi* where friedelan-2α,3β-diol was found. In addition, three new cycloartane triterpenes, lithocarpolone (21,24-epoxy-24-hydroxymethyl-cycloartan-3-one), lithocarpdiol (21,24-epoxy-24-hydroxymethyl-cycloartan-3β-ol), and 24-methylenecycloartan-3β,21-diol were found in *L. polystachya*, and their structures determined.

INTRODUCTION

OF THE three genera constituting the Fagaceae in Hong Kong, *Quercus*[1,2] and *Castanopsis*[3] have already been shown to contain triterpenes of the friedelane, D:B-friedo-oleanane, ursane, lupane and hopane groups. We now present the results of a complementary study of five species of the remaining genus, *Lithocarpus*, and also provide evidence for the structures of three new triterpenes from *L. polystachya*.

RESULTS

All five *Lithocarpus* species examined (viz *L. cornea*, *L. glabra*, *L. hancei*, *L. harlandi* and *L. polystachya*) contain friedelin, friedelan-3β-ol, taraxerol (occurring also as the acetate in *L. cornea*), and β-amyrin (Table 1). Glutinol was isolated from all species except *L. harlandi* which contains instead friedelan-2α,3β-diol (pachysandiol-A),[4] previously reported to occur only in *Pachysandra terminalis*.[4] *L. polystachya* also yielded three cycloartane triterpenes (**1**), (**3**) and (**5**), the structures of which were determined.

Two of the triterpenes are closely related; upon reduction lithocarpolone (**1**), $C_{31}H_{50}O_3$, (ν_{max} 1710 cm^{-1}) yields lithocarpdiol (**3**), $C_{31}H_{52}O_3$, (no C=O absorption). These two triterpenes each contains a primary hydroxy group of the type $\geqslant C{-}CH_2OH$ (AB q at δ 3·4, *J* 11 Hz[†]), and on acetylation yield lithocarponone acetate (**2**) (AB q at δ 4·1; no OH

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[†] For full NMR data, see Table 2. Measurements are in $CDCl_3$ solutions unless otherwise stated.

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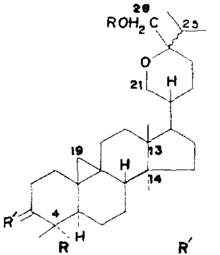
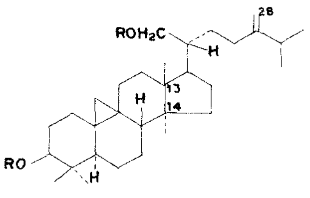
TABLE 1. YIELDS OF TRITERPENES FROM LEAVES OF *Lithocarpus* SPECIES (% DRY WEIGHT)

	L. cornea	*L. glabra*	*L. hancei*	*L. harlandi*	*L. polystachya*
Taraxeryl acetate	0·0005				
Friedelin	0·10	0·0003	0·071	0·091	0·005
Friedelan-3β-ol	0·01	0·0003	0·016	0·067	0·001
Glutinol	0·01	0·040	0·001		0·017
β-Amyrin	0·003	0·007	0·001	0·002	0·003
Taraxerol	0·09	0·12	0·0004	0·004	0·088
Friedelan-2α,3β-diol				0·003	
Lithocarpolone					0·005
Lithocarpdiol					0·001
24-Methylenecycloartan-3β,21-diol					0·002

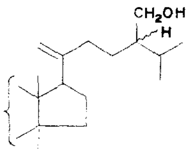
absorption) and lithocarpdiol diacetate (**4**) (AB q at δ 4·1, *J* 11·5 Hz; 1-H multiplet at δ 4·6) respectively. Common to both triterpenes is a cyclopropane ring of the type $>C{-}(CH_2){-}C<$ (AB q near δ 0·6, *J* 4 Hz) and an isopropyl group. Evidence for the latter is derived from NMR decoupling experiments (in C_6D_6). Thus lithocarpdiol diacetate (**4**) gives rise to two methyl doublets both of which collapse to singlets upon saturation of a heptet at δ 2·4.



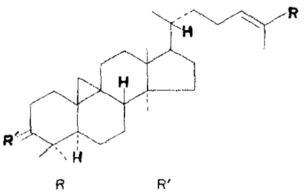
	R	R'
(**1**)	H	O
(**2**)	Ac	O
(**3**)	H	α-H, β-OH
(**4**)	Ac	α-H, β-OAc
(**7**)	$MeC_6H_4SO_2-$	O



(**5**) R = H
(**6**) R = Ac



(**5a**)



	R	R'
(**9**)	Me	O
(**10**)	COOMe	O
(**11**)	COOH	O
(**12**)	Me	α-H,β-OAc
(**13**)	COOMe	α-H,β-OH
(**14**)	COOH	α-H,β-OH

The remaining oxygen atom in the structure of lithocarpolone (and lithocarpdiol) is assigned to an ether function of the type $>CH.CH_2.O.C\lessgtr$. Thus in the NMR spectra of lithocarpolone, lithocarpdiol and their respective acetates is a 2-H multiplet at δ 3·2–3·9. For lithocarpolone acetate the signal constitutes the AB part of an ABX system (Table 2) and it simplifies to an AB quartet (*J* 11·5 Hz) upon double irradiation at δ 1·7.

The third triterpene (**5**), $C_{31}H_{52}O_2$, also has a cyclopropane ring of the type $>C{-}(CH_2){-}C<$ and an isopropyl group. The latter gives rise to two superimposing methyl doublets detected when the 60 and 100 MHz spectra were compared. Other structural features are a terminal methylene (υ_{max} 890 cm^{-1}; δ 4·70, 4·74) and two hydroxy groups. One hydroxyl is secondary (1-H multiplet at δ 3·3 shifting to 4·6 on acetylation), and the other is primary and of the type $>CH.CH_2.OH$ (2-H multiplet at δ 3·7, becoming on acetylation AB of ABX at δ 4·1) (Table 2).

TABLE 2. CHEMICAL SHIFTS* (AND COUPLING CONSTANTS IN Hz) OF TRITERPENES OF *L. polystachya*

	Lithocarpolone (**1**)	Lithocarpolone acetat (**2**)	Lithocarpolone tosylate (**7**)	Lithocarpdiol (**3**)	Lithocarpdiol diacetate (**4**)	24-Methylene-cycloartan-3β-21-diol (**5**)	24-Methylene-cycloartan-3β,21-diol diacetate (**6**)
H-3α				~3·3 m†	4·57 (J_{AX} + J_{BX} = 15)	3·92 (J_{AX} + J_{BX} = 15·5)	4·58 (J_{AX} + J_{BX} = 13)
H-19	0·59 *d* (*J*, 4)	0·59 *d* (*J*, 4)	0·6 *d* (*J*, 4)	0·35 *d* (*J*, 4)	0·35 *d* (*J*, 4)	0·31 *d* (*J*, 4)	0·35 *d* (*J*, 4)
H-19	~0·8 m†	0·78 *d* (*J*, 4)	†	0·56 *d* (*J*, 4)	0·57 *d* (*J*, 4)	0·56 *d* (*J*, 4)	0·59 *d* (*J*, 4)
H-21	~3·3 m†	3·34 *q* (*J*, 11·5, ~2)	~3·2 m	~3·3 m†	3·30 *q* (*J*, 11·5, ~2)	~3·7 m	3·94 *q* (*J*, 11, 5·5)
H-21	3·83 m	3·82 *q*† (*J*, 11·5, 8)	~3·7 m	3·8 m	3·85 *q* (*J*, 11·5, 8)	~3·7 m	4·22 *q* (*J*, 11, 2·5)
H-25	†	†	†	†	2·43 heptet	†	†
H-28	3·30 *d* (*J*, 11)	3·94 *d* (*J*, 11·5)	3·94	3·25 *d* (*J*, 11)	3·96 *d* (*J*, 11·5)	4·70	4·67
H-28	3·58 *d* (*J*, 11)	4·15 *d* (*J*, 11·5)	3·97	3·55 *d* (*J*, 11)	4·14 *d* (*J*, 11·5)	4·74	4·73
AcO		2·10			2·05 2·09		2·05 2·05
TsO			2·45 (3H) 7·35 *d* (*J*, 8) 7·85 *d* (*J*, 8)				

* Relative to $SiMe_4$; $CDCl_3$ solution.
† Partially obscured by other peaks.

Biogenetic considerations suggest that the *L. polystachya* triterpenes, each with 31 carbon atoms and a cyclopropane ring, are 24-methylcycloartanes with oxygen functions at C-3. Confirmation comes from a study of the NMR signals of their methyl groups.[5,6] In

TABLE 3. NMR FREQUENCIES* OF METHYL GROUPS (Hz) OF CYCLOARTANE TRITERPENES

	Substituents at C-3	4α-Me	4β-Me	14α-Me	13β-Me	25-Me† (doublets, *J* 7)
Cycloartenone (**9**)	(3-oxo)	64·5	62	54·5	60	
Methyl maniferonate (**10**)	(3-oxo)	65	62	54	59	
Mangiferonic acid (**11**)	(3-oxo)	65	62	54	60	
Lithocarpolone (**1**)	(3-oxo)	65	62	53·5	62	50·5, 53·5
Lithocarpolone acetate (**2**)	(3-oxo)	65·5	62·5	54	61·5	55, 56·5
Lithocarpolone tosylate (**7**)	(3-oxo)	65·5	62	53	58·5	49·5, 51·5
Methyl maniferolate (**8**)	β-OH	58·5	49	54	58·5	
Mangiferolic acid (**14**)	β-OH	58	49	54	58	
Lithocarpdiol (**3**)	β-OH	58	48·5	53·5	60	51, 53·5
24-Methylenecycloartan-3β,21-diol (**5**)	β-OH	58	49	55	60	62, 62 (65·5, 65·5)
Cycloartenyl acetate (**12**)	β-OAc	51	54	54	58	
Lithocarpdiol diacetate (**4**)	β-OAc	51	53·5	53·5	60	55, 56·5
24-Methylenecyloartan-3β,21-diol diacetate (**6**)	β-OAc	51	53·5	55	60	62, 62 (64, 64)

* Relative to $SiMe_4$ at 60 MHz but measured also at 100 MHz; $CDCl_3$ solution.
† Data listed only for *L. polystachya* triterpenes; frequencies in parenthesis refer to C_6D_6 solution.

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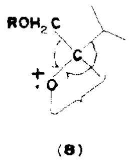
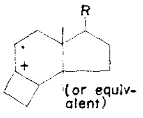
Table 3, the methyl resonance frequencies of some cycloartane compounds and of the *L. polystachya* triterpenes and their derivatives are assigned[6] and compared. As is expected for compounds with identical skeletons, the methyl group at position 4α or position 4β gives rise to a constant resonance frequency (±0·5 Hz at 60 MHz) for a specific substituent at C-3; likewise, the methyl group at 14α, being remote from both ring *A* and the side-chain, resonates within a narrow range (54 + 1 Hz at 60 MHz) for all 13 compounds listed.

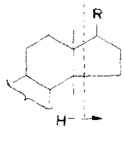
Cycloartane triterpenes are also characterized by MS fragmentations initiated by the 9:19-cyclopropane ring, and which result in an ion (**a**) of *m/e* independent of the substitution pattern in ring *A*.[7,8] The MS of the *L. polystachya* triterpenes and their derivatives conform to this pattern (Table 4) and show three groups of ions, (i) the M^+ and ions derived from it by simple losses, (ii) ion (**a**) and/or ions derived therefrom, (iii) ions due to cleavage of the side-chain (sometimes accompanied by rearrangement of one or two hydrogen atoms)[9] and of ring *D* (see **b**).[10]



(**8**)
(R=H or Ac)



(a)



(b)

TABLE 4. 70 eV FRAGMENT IONS (*m/e*)* OF *L. polystachya* TRITERPENES

Assignments [R=H for (**1**), (**3**) and (**5**); R=Ac for (**2**), (**4**) and (**6**)]	Lithocarpolone (**1**)	Lithocarpolone acetate† (**2**)	Lithocarpdiol (**3**)	Lithocarpdiol diacetate† (**4**)	24-Methylene-cycloartan-3β,21-diol (**5**)	24-Methylene-cycloartan-3β,21-diol diacetate (**6**)
M^+	470	512	472	556	*456*	540
→M–Me	455	497	457	541‡	441‡	525‡
→ M–CH(Me)₂	*427*	*469*	*429*	*513*	413‡	497
→M–ROH	452	452	454	*496*‡	*438*‡b	*480*‡
M–Me–ROH				*481*‡	*423*‡	*465*‡
M–Me–2ROH					405‡	405
M–2ROH					420	420‡
M–CH₂OR	*439*b	*439*b	*441*‡b	*483*b	425	
M–CH₂OR–ROH			423‡	423‡	407	
M–CH(Me)₂–ROH	409‡	409‡	411‡§	*453*‡§	*395*‡§	*437*§
M–CH(Me)₂–ROH–H₂O		391				
M–CH(Me)₂–2ROH			393	393‡		
M–C₅H₉–ROH					369‡	411‡
M–C₅H₉–2ROH					351	351
(a)		374	332	374	*316*	358
(a)–Me					301	343
(a)–CH(Me)₂	289	331	289	*331*		
(a)–ROH						298‡
(a)–CH₂OR	301	301	*301*‡	*301*	285	285
M-side-chain	313 312 311	313 312 311	315 314 313	357 356 355	315 314 313	357 356 355
M-side chain–ROH			297	297	297	297
(b)	271	271	273	315	273‡	315
(b)–ROH			255	255	255	255

* Ions of rel. abundance > 20% are shown in italics; b = base peak.
† Confirmed by accurate mass measurements.
‡ m* observed for transition.
§ Also derived from M^+-ROH ion (m* observed).

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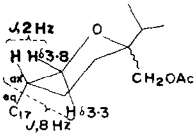
For lithocarpolone, lithocarpdiol and their acetates, the three most abundant ions correspond to the loss of CH_2OR (R=H or Ac) or of isopropyl (but not of both groups) from the M^+ and to the loss of CH_2OR from ion (**a**) (Table 4). The observed ease of cleavage shows that these two groups are located α to the ether oxygen atom as is indicated in partial structure (**8**).* Structures (**1**) and (**3**) thus represent lithocarpolone and lithocarpdiol respectively.

Of the two alternative structures (**5**) and (**5a**) for the third triterpene, we favour the former (viz 24-methylenecycloartan-3β,21-diol). For (**5**) but not for (**5a**), the two terminal methyl groups are remote from any asymmetric centre and from a hydroxy group, and are expected to be equivalent magnetically and not deshielded on acetylation. The result in Table 3 (right column) shows that this expectation was substantiated when the triterpene and its diacetate were examined in two solvents (and at two resonance frequencies).

For confirmation of structure (**5**) the following decoupling experiment (in C_6D_6) was carried out. Irradiation at δ 2·5 resulted in the collapse of the methyl doublets (see above) and also caused sharpening of the signal due to the vinyl protons (width-at-half-height, 2·8 → 1·6 Hz) as the result of reduction of allylic coupling.

24-Methylenecyloartan-3β,21-diol and lithocarpdiol are assigned a 3β configuration based on NMR data (Table 2). For the latter compound the configuration is also supported from the result of borohydride reduction of the corresponding ketone.

The stereochemistry of the side-chain shown in (**1**)–(**6**) is proposed on the assumption that C-20 retains the configuration found in cycloartane triterpenes, and in the cases of (**1**)–(**4**), on the relative magnitude of the chemical shifs and vicinal coupling constants of the two protons at C-21[11] (see (**15**) and Table 2).



(**15**)

DISCUSSION

As the previous[1–3] and present work have covered nearly half of the 30 or so species of the Fagaceae indigenous to Hong Kong, it is appropriate to comment on the salient features of the triterpene distribution which have emerged. In Table 5 are summarized the results of the work in Hong Kong[1–3] and elsewhere.[12–23] Of the five genera which have

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* Partial structure (**8**) is also supported by the observation, in the case of lithocapdiol diacetate, of a nuclear Overhauser effect (11% enhancement) between the methylene and methyl protons of the CH_2OAc and isopropyl groups respectively.

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been examined, only limited data are available on *Castanea* and *Fagus*. The other three genera all produce triterpenes of the D:A–friedo- oleanane group. In particular friedelin and/or the corresponding 3-alcohols occur in all but one species of the 23 species of *Castanopsis*, *Quercus* and *Lithocarpus* studied. The genus *Lithocarpus* is characterized by the prevalent occurrence of D:B–friedo-, D–friedo-, and unrearranged oleanane triterpenes, which are significantly less common in *Quercus* and rare in *Castanopsis*. On the other hand, the genus *Castanopsis* is characterized by triterpenes of the hopane, lupane and ursane groups. It appears that the genus *Quercus* lies chemotaxonomically between *Castanopsis* and *Lithocarpus*.

TABLE 5. DISTRIBUTION OF TRITERPENES IN THE FAGACEAE (PLANT SPECIES IN PARENTHESIS REFER TO THIS OR EARLIER HONG KONG WORK)

Triterpene group	Triterpenes isolated	*Castanea sativa*[12]	*Castanopsis*						*Fagus*		*Quercus*												*Lithocarpus*				
			(C. concinna)[3]	*(C. cuspidata)*[3]	*(C. eyrei)*[3]	*(C. fabri)*[3]	*(C. fissa)*[3]	*(C. hickelii)*[3]	*F. sylvatica*[13]	*F. taurica*[14]	*Q. acutissima*[15]	[illegible]	*(Q. championi)*[1,2]	*(Q. glauca)*[1]	*Q. ilex*[16]	*Q. incana*[19]	[illegible]	*Q. pachyphlla*[1]	*Q. petreae*[18]	*Q. robur*[19–21]	*Q. sessilis*[22]	[illegible]	*(L. cornea)*	*(L. glabra)*	*(L. hancei)*	*(L. harlandi)*	*(L. polystachya)*
Hopane	Hopan-22-ol-3-one				+			+																			
	Hopan-3β,22-diol				+																						
	Hop-17(21)-en-3β-ol (and/or acetate)												+														
Ursane	α-Amyrin														+												
	Taraxasterol					+		+																			
	Ursolic acid	+																									
Lupane	Lupenone										+																
	Lupeol	+		+			+								+					+	+						
	Betulin	+							+																		
	Betulinic acid (and/or methyl ester acetate)								+																		
D:A-Friedo-oleanane	Friedelan-28-ol-3-one		+								+																
	Friedelan-3α-ol (and/or acetate)			+								+	+				+		+	+		+					
	Friedelan-3β-ol		+	+	+	+	+	+				+	+	+			+						+	+	+	+	+
	Friedelin		+	+	+	+	+	+			+	+	+	+	+	+		+	+	+		+	+	+	+	+	+
	Friedelan-2α,3β-diol																									+	
D:B-Friedo-oleanane	Glutinol					+														+			+	+	+		+
	Glutinone																			+							
D-Friedo-oleanane	Taraxerol (and/or acetate)																			+	+	+	+	+	+	+	+
Oleanane	Oleanolic acid														+			+									
	β-Amyrenone										+																
	β-Amyrin (and/or acetate)								+				+		+						+		+	+	+	+	+
Arborane	Isoarborinyl acetate												+														
Dammarane	20-Hydroxydammar-24-en-3-one																			+							
Cyclo-artane	24-Methylenecycloartan-3β,21-diol (**5**)																										+
	Lithocarpolone (**1**)																										+
	Lithocarpdiol (**3**)																										+
	Cycloartenylacetate								+																		

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EXPERIMENTAL

M.ps were uncorrected. Optical rotations and IR spectra were measured in $CHCl_3$ solns and Nujol mulls respectively. MWs were recorded from MS. MS (Table 4) were recorded at 70 eV. and mass matching was performed in conjunction with a DS-30 data-processing system. Isolated compounds were identified by m.m.p. and IR spectral comparisons with authentic samples. Petrol. refers to the fraction of b.p. 60–80°.

Isolation of triterpenes. Dried and milled leaves of plants collected in Hong Kong were cold extracted twice with petrol. The residue obtained on evaporation of the combined extracts was chromatographed on 15–20 × its weight of Al_2O_3 using gradient elution with C_6H_6–petrol, and then with $CHCl_3$–C_6H_6.

Lithocarpus cornea, *L. glabra*, *L. hancei*, *L. harlandi*, and *L. polystachya* each gave the following compounds (in yields shown in Table 1). (a) Friedelin, m.p. 262–264° (from petrol), ν_{max} 1720 cm^{-1}. (b) Friedelan-3β-ol, m.p. 282–285° (from petrol), acetate, m.p. 290–291° (from C_6H_6). (c) Glutinol, m.p. 210–212° (from petrol), ν_{max} 3480 cm^{-1}, acetate, m.p. 190–192°. (d) β-Amyrin, m.p. 198–200° [from $(Me)_2CO$], ν_{max} 3300 cm^{-1}; acetate, m.p. 238–240° (from $CHCl_3$–MeOH), ν_{max} 1740, 1250 cm^{-1}. (e) Taraxerol, m.p. 283–284° (from C_6H_6), ν_{max} 3500, 1640 cm^{-1}; acetate, m.p. 309–313° (from C_6H_6–petrol), ν_{max} 1740, 1250 cm^{-1}. Taraxeryl acetate was also isolated from *L. cornea*. From the polar fraction of the triterpene mixture from *L. harlandi* was isolated friedelan-2α,3β-diol (pachysandiol-A)[4] forming needles from $(Me)_2CO$, m.p. 282–285°, ν_{max} 3500 cm^{-1}, diacetate, m.p. 235–236° [from $(Me)_2CO$].

Isolation of cycloartane triterpenes from L. polystachya *and conversion to acetates.* In the chromatographic separation of the triterpenes from *L. polystachya* leaves, after removal of the substances recorded above, further elution with $CHCl_3$–C_6H_6 afforded (in yields shown in Table 1): *Lithocarpolone* (**1**), needles from $(Me)_2CO$, m.p. 190–192°, $[\alpha]_D$ + 28°, ν_{max} 3450, 1710 cm^{-1} (Found: C, 79·5; H, 10·7. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·7%). 24-*Methylenecycloartan-3β,21-diol* (**5**), needles from $(Me)_2CO$–MeOH, m.p. 165–168°, $[\alpha]_D$ + 42°, ν_{max} 3350, 1650, 890 cm^{-1} (Found: C, 78·5; H, 11·4%; MW 456. $C_{31}H_{52}O_2.H_2O$ requires C, 78·4; H, 11·5%. $C_{31}H_{52}O_2$ requires MW 456). *Lithocarpdiol* (**3**), needles from $(Me)_2CO$, m.p. 179–180°, $[\alpha]_D$ + 54°, ν_{max} 3350 cm^{-1} (Found: C, 77·1; H, 11·2%; MW 512. $C_{31}H_{52}O_3.1/2H_2O$ requires C, 77·4; H, 11·1%. $C_{31}H_{52}O_3$ requires MW 512).

Each of the above three triterpenes (40 mg) were treated for 5 hr with $(Ac)_2O$ (8 ml) and C_5H_5N (1 ml) under reflux, and worked up to give: *Lithocarpolone acetate* (**2**), needles from MeOH, m.p. 144–145°, $[\alpha]_D$ +37°, ν_{max} 1745, 1710, 1240 cm^{-1} (Found: C, 76·6; H, 9·8%; MW 512·387. $C_{33}H_{52}O_4$ requires, C, 77·3; H, 10·2%; MW 512·386). 24-*Methylenecycloartan-3β,21-diol diacetate* (**6**), needles from $(Me)_2CO$–MeOH, m.p. 137–139°, $[\alpha]_D$ + 50°, ν_{max} 1740, 1635, 1245, 890 cm^{-1} (Found: C, 77·9; H, 10·3. $C_{35}H_{46}O_4$ requires C, 77·8; H, 10·4%). *Lithocarpdiol acetate* (**4**), needles from EtOH, m.p. 179–180°, $[\alpha]_D$ + 64°, ν_{max} 1740, 1245 cm^{-1} (Found: MW 556·412; $C_{35}H_{54}O_5$ requires MW 556·413).

Reactions of lithocarpolone. Lithocarpolone was stable to BF_3 etherate complex at 0°. On overnight treatment with excess toluene-*p*-sulphonyl chloride in C_5H_5N at 0°, lithocarpolone was converted to *lithocarpolone toluene*-p-*sulphonate* (**7**), m.p. 207–209°, ν_{max} 1705, 1605, 1190, 1175 cm^{-1}.

To lithocarpolone (58 mg) in dioxan (3 ml) was added $NaBH_4$ (337 mg) in MeOH (15 ml), and the mixture was refluxed for 2 hr. After removal of most of the solvent under vacuum, the mixture was acidified with 50% aq. HOAc. The precipitated product recrystallized from $(Me)_2CO$ consisted of a mixture of 3-alcohols. The major epimer, isolated by preparative TLC was identical to lithocarpdiol (**3**) isolated from the plant.

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