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ACIDIC TRITERPENOIDS FROM NINE *LITHOCARPUS* SPECIES OF HONG KONG

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Key Word Index—*Lithocarpus* species; Fagaceae; triterpene acids of the lupane, oleanane and ursane series; olean-12-en-1,3-dione.

Plants. Lithocarpus cornea (Lour.) Rehd., *L. elizabethae* (Tutch.) Rehd., *L. glabra* (Thunb.) Nakai, *L. haipinii* Chun., *L. hancei* (Benth.) Rehd., *L. harlandi* (Hance) Rehd., *L. irwinii* (Hance) Rehd., *L. litchioides* Chun., and *L. polystachya* (Wall.) Rehd. *Previous work.* Neutral triterpenoids and sterols [1,2]; lithocarpic lactone from *L. litchioides* and *L. irwinii* [3]; eight new triterpenoids from *L. cornea* [4]. On sister species: *L. attenuata*, acidic triterpenoids [5].

Present work. The ethanol extracts of both the stems and leaves of each plant were examined separately according to the method reported for *L. attenuata* [5].

The stems of all the nine species were found to contain triterpene acids (isolated as their methyl esters), while such compounds could not be isolated from the leaves of any of the species (cf. *L. atttenuata* [5]). Besides oleanolic acid from four and betulinic acid from all species except *L. cornea*, other acids of the oleanane group were obtained: acetyl oleanolic acid from *L. hancei*, and cincholic, morolic, and acetyl morolic acids from *L. cornea*. This is the first report of acetyl morolic acid as a natural product. Among compounds of the ursane series, ursolic acid was found in *L. elizabethae* and *L. irwinii*, while the former also yielded acetyl ursolic and quinovic acids. Olean-12-en-1,3-dione which was first isolated from *L. attenuata* [5] as a mixture with 3-methoxyoleana-2,12-dien-1-one formed by partial methylation of the dione in the enol form, was also found in *L. cornea* as a similar mixture. From the above results, it appears that the stems of *Lithocarpus* species are characteristic in yielding triterpene acids. We have also performed similar investigations on the closely related *Castanopsis* species of Hong Kong which have been reported to contain neutral triterpenoids [6–8], and found that neither the leaves nor stems of any of these yielded triterpene acids.

The distribution of triterpene acids in the nine *L.* species together with those reported in *L. attenuata* [5] are listed in Table 1.

EXPERIMENTAL

IR spectra were recorded for KBr discs, UV spectra in 95% EtOH and optical rotations in $CHCl_3$ solution. Light petrol had bp 60–80°. All compounds were identified by TLC, mmp and IR spectral comparisons with authentic samples.

Extraction, isolation and methylation of acidic mixture. Air-dried stems of each plant were extracted with 95% ethanol after removal of less polar substances with light petrol, and the acidic mixture from the ethanol extract was isolated and methylated as for *L. attenuata* [5]. Air-dried leaves of all nine plants were examined in the same way, but no acidic material could be obtained from any of the extracts.

L. cornea. Stems (43·5 kg), methylated product (43·7 g) and alumina (1 kg) were used. Elution with light petrol gave a solid which was recrystallized from the same solvent to give plates of methyl acetyl morolate (0·01 g), mp 263–265°, $[\alpha]_D$ + 40·0° (Found: M^+ 512. Calc. for $C_{33}H_{52}O_4$, M^+ 512). IR ν_{max}: 1740, 1250 (OAc), 1730, 1195 (COOMe), 1650, 845 cm^{-1} (>C=CH–); then prisms of 3-methoxyoleana-2,12-dien-1-one (0·02 g), mp 234–236° (from light petrol), $[\alpha]_D$ + 223·5°, IR ν_{max}: 1675, 1615 (>C=C–C=O), 1196 (vinyl ether), 832 cm^{-1} (>C=CH–), UV λ_{max}: 251 nm (ε 12,000); and finally needles of olean-12-en-1,3-dione (2 mg), mp's 120–125°, 205–208° (from light petrol), IR ν_{max}: 3400 (OH), 1600, 1575 cm^{-1} (>C=C–C=O). Elution with light petrol–C_6H_6 (1:1) gave needles of methyl morolate (0·015 g), mp 231–232° (from C_6H_6), $[\alpha]_D$ + 35·0°, M^+ 470, IR ν_{max}: 3580 (OH), 1720, 1225 (COOMe), 1650, 850 cm^{-1} (>C=CH–), (acetate mp 262–265°, identical with methyl acetyl morolate isolated); then needles of methyl oleanolate (0·03 g), mp 198–201° (from C_6H_6), $[\alpha]_D$ + 70·1°, IR ν_{max}: 3380 (OH), 1730, 1160 (COOMe), 3030, 1650, 850 cm^{-1} (>C=CH–). Elution with C_6H_6 gave plates of dimethyl cincholate (0·012 g), mp 216–217° (from C_6H_6), $[\alpha]_D$ + 107·0°, IR ν_{max}: 3600 (OH), 1740, 1720, 1200 (2 × COOMe), 1660, 840 cm^{-1} (>C=CH–).

L. elizabethae. Stems (4 kg), methylated product (6 g) and alumina (130 g) were used. Elution with light petrol gave plates of methyl acetyl ursolate (0·01 g), mp 245–247° (from light petrol), $[\alpha]_D$ + 64·0°, IR ν_{max}: 1740, 1250 (OAc), 1730, 1200 (COOMe), 1650, 810 cm^{-1} (>C=CH–). Elution with light petrol–C_6H_6 (1:1) gave prisms of methyl betulinate (0·05 g), mp 228–230° (from $CHCl_3$), $[\alpha]_D$ + 7·0°, IR ν_{max}: 3550 (OH), 1720, 1174 (COOMe), 3080, 1650, 880 cm^{-1} (>C=CH_2), and needles of methyl ursolate (0·015 g), mp 168–170° (from light petrol, $[\alpha]_D$ + 63·0°, IR ν_{max}: 3350 (OH), 1740, 1200 (COOMe), 1640, 820 cm^{-1} (>C=CH–). Elution with C_6H_6 gave long needles of dimethyl quinovate (0·015 g), mp 181–182° (from $CHCl_3$), $[\alpha]_D$ + 120·0°, IR ν_{max}: 3590 (OH), 1735, 1710, 1205 (2 × COOMe), 1655, 840 cm^{-1} (>C=CH–).

Table 1. Acidic Triterpenoids from ten *Lithocarpus* species

Group	Compounds isolated	Species
Oleanane	Olean-12-en-1,3-dione	*L. attenuata*, *L. cornea*
	Acetyl oleanolic acid	*L. hancei*
	Oleanolic acid	*L. attenuata*, *L. cornea*, *L. hancei*, *L. harlandi*, *L. litchioides*
	Cincholic acid	*L. cornea*
	Morolic acid	*L. cornea*
	Acetyl morolic acid	*L. cornea*
Ursane	Acetyl ursolic acid	*L. elizabethae*
	Ursolic acid	*L. elizabethae*, *L. irwinii*
	Quinovic acid	*L. elizabethae*
Lupane	Betulinic acid	All species except *L. cornea*

L. glabra. Stems (5 kg), methylated product (4 g) and alumina (100 g) were used. Elution with light petrol gave needles of methyl betulinate (0·3 g).

L. haipinii. Stems (14 kg), methylated product (10 g) and alumina (200 g) were used. Elution with light petrol gave methyl betulinate (0·3 g).

L. hancei. Stems (9 kg), methylated product (6 g) and alumina (200 g) were used. Elution with light petrol gave prisms of methyl acetyl oleanolate (0·01 g), mp 224–225° (from light petrol), $[\alpha]_D$ + 76·0°, IR ν_{max}: 1745, 1240 (OAc), 1730, 1208 (COOMe), 1660, 820 cm^{-1} (>C=CH–). Elution with light petrol–C_6H_6 (1 : 1) gave methyl betulinate (0·01 g) and then methyl oleanolate (5 mg).

L. harlandi. Stems (10 kg), methylated product (2 g) and alumina (50 g) were used. Elution with light petrol–C_6H_6 (1 : 1) gave methyl betulinate (0·012 g) and methyl oleanolate (0·02 g).

L. irwinii. Stems (21·5 kg), methylated product (7 g) and alumina (200 g) were used. Elution with light petrol–C_6H_6 (1 : 1) gave methyl betulinate (0·09 g) and then methyl ursolate (0·02 g).

L. litchioides. Stems (11 kg), methylated product (3 g) and alumina (70 g) were used. Elution with light petrol–C_6H_6 (1 : 1) yielded methyl betulinate (0·07 g) and methyl oleanolate (0·1 g).

L. polystachya. Stems (7·2 kg), methylated product (3 g), alumina (60 g) were used. Elution with light petrol–C_6H_6 (1 : 1) gave methyl betulinate (0·03 g).

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TRITERPENES TETRACYCLIQUES DU *SIMAROUBA AMARA*

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Simarouba amara Aubl. est assez répandu en Guyane. Les écorces de cet arbre, connu sous le nom d'"Assoumaripa", sont utilisées par la population locale pour diverses médications. Nous avons étudié les écorces de tiges, récoltées en 1973 par M. J. J. de Granville du Centre O.R.S.T.O.M. de Cayenne. L'identification de l'espèce a été faite par le Dr P. Boiteau qui avait examiné un échantillon botanique envoyé par M. H. Jacquemin.

Antérieurement [1], nous avions isolé le simarolide **1**—un des premiers et rares quassinoïdes dont le squelette de base est en C_{25} [2]—à partir des écorces de racines de *Simarouba amara*, originaire d'Amazonie. Contrairement à ces écorces, celles de tiges provenant de Guyane ne sont pas amères et aucun quassimoïde n'en a pu être extrait. Nous en avons cependant isolé deux triterpènes tétracycliques de la série du $\Delta^{7,8}$-tirucallol; leur présence dans une Simarubacée présente un certain intérêt du fait que les composés de cette famille sont considérés comme les précurseurs biogénétiques des quassinoïdes [2]. Le présent mémoire expose les résultats qui conduisent à attribuer les structures **2** et **3** à ces deux triterpènes. Le premier est un triterpène nouveau et le deuxième, mentionné dans la littérature [3], n'avait pas encore été isolé d'une source naturelle.

La chromatographie de l'huile obtenue par extraction des écorces permet d'isoler, en plus du sitostérol, deux composés cristallisés.

Triterpène **2**. $C_{30}H_{46}O_2$. Son spectre IR ($CHCl_3$), dépourvu de bandes OH, montre des bandes C=O à 1710 et 1730 cm^{-1}. Le spectre de RMN du proton du composé **2** révèle la présence d'éléments structuraux suivants: groupement isopropylidène = CMe_2 cinq groupes méthyles, groupement –CH–CHO et deux protons oléfiniques du type >C=CH–CH_2–. Les déplacements chimiques de ces protons oléfiniques et l'allure de leurs signaux sont en bon accord avec leur localisation en C-24 et C-7. La présence de deux double liaisons, $\Delta^{7,8}$ et $\Delta^{24,25}$, est confirmée par l'examen de son spectre de RMN du ^{13}C.

La courbe de dichroisme circulaire ($\Delta\epsilon_{298\,nm} = -0{,}9$) du composé **2** est tout à fait comparable à celle de céto-3,Δ^7 triterpénoïdes [4]. Les données de la spectrométrie de masse prouvent la structure de la chaîne latérale et plus particulièrement la position de la fonction aldéhyde en C-20. Le spectre de masse du composé **2** montre, en effet, en plus de l'ion moléculaire à *m/e* 438, des pics significatifs à *m/e* 423, 356, 341, 297, 287, 273 et 271. Ces pics peuvent être assignés aux ions formés