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# TERPENES OF *DIPTEROCARPUS* AND *DOONA* SPECIES*†

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**Key Word Index**—*Dipterocarpus hispidus*; *Dipterocarpus zeylanicus*; *Doona congestiflora*; *Doona macrophylla*; Dipterocarpaceae; triterpenes; structural analysis.

**Abstract**—From the resins of *Dipterocarpus hispidus*, *Dipterocarpus zeylanicus* and *Doona macrophylla*, asiatic (2α,3β,23α-trihydroxyurs-12-en-28-oic) and 2α,3β-dihydroxyurs-12-en-28-oic acids have been isolated. The resin of *Doona macrophylla* contains ursolic acid and that of *Doona congestiflora* asiatic acid, 20β-hydroxy-3-oxo dammar-23-ene (Dipterocarpol) and a dihydroxyolean-12-en-28-oic acid. The bark of *Dipterocarpus hispidus* contains betulinic acid, dipterocarpol, and 3β,20β-dihydroxydammar-23-ene (dammarenediol 20S) whilst the timber contained dipterocarpol and asiatic acid.

## INTRODUCTION

About 550 plant species belonging to the family Dipterocarpaceae are widely distributed in the rain forests of South East Asian countries, India and Ceylon. In Ceylon there are about 48 species belonging to 10 genera. In recent surveys the distribution of sesqui- and tri- terpenoid constituents of over 70 samples of resins from 6 genera including Ceylonese plants from the genera *Doona* Thw., and *Dipterocarpus* Gaertn. f have been studied [1–4]. The isolation of triterpenoid constituents from the resins of *Dipterocarpus hispidus* Thw. *Dipterocarpus zeylanicus* Thw., *Doona congestiflora*‡ Thw., and *Doona macrophylla* Thw., is now reported. Work on the bark and timber extractives of *Dipterocarpus hispidus* Thw., is also described.

* Under the revision of the flora of Ceylon project, Dr. P. Ashton has recently reclassified the Dipterocarpaceae of Ceylon (private communication).

† Part 13 in the series "Chemical Investigation of Ceylonese Plants". For Part 12 see G. Pavanasasivam and M. U. S. Sultanbawa (1975) *J. Chem. Soc. Perkin I* (in press).

‡ Diaz, Ourisson and Bisset [4] report work on the resins of the Ceylonese species *Doona congestiflora* Thw. and *Doona congestifolia* Thw. As the plant *Doona congestifolia* is not found in Sri Lanka (Ceylon) it is to be assumed that *Doona congestifolia* Thw. referred to in the report refers to *Doona congestiflora* Thw.

## RESULTS AND DISCUSSION

Chemical analyses of the neutral fraction of the resin of *Dipterocarpus hispidus*. by Bisset *et al.* [2] revealed the presence of 8 compounds. It has been shown in the present study that dipterocarpol (20β-hydroxy-3-oxodammar-23-ene) the major component of the neutral fraction, is present to the extent of *ca* 48%. The mixture of sesquiterpenoids, caryophyllene, humulene and alloaromadendrene was the next most abundant (*ca* 24%) and the compounds were present in the ratio 7:10:3 respectively. Ocotillone 20R (24-hydroxy-20α,23-epoxydammaran-3-ene) and ocotillone 20S were isolated in yields of *ca* 0·05%, and *ca* 0·04% respectively.

The petrol insoluble fraction of the resin was shown to contain one major and one minor component and they were separated by column chromatography. The least polar of the two (minor component *ca* 0·13%) was shown to be a terpenoid (Liebermann Burchard test) of molecular formula $C_{30}H_{48}O_4$. The IR spectrum indicated the presence of an OH group (3400 $cm^{-1}$) and an angular $CO_2H$ group (1692 $cm^{-1}$). Facile acetylation indicated the absence of a tertiary OH group, and the MW of the acetate showed the compound to be a dihydroxy acid. The PMR

signal at $\tau$ 4·56 of the dihydroxy acid and at $\tau$ 4·76 of the diacetate was due to the C-12 olefinic proton (1H, *m*, $W_{\frac{1}{2}} = 8$ Hz). The characteristic peaks at *m/e* 248, 203 and 133 in its MS indicated the dihydroxy compound to be a Δ12-ursene or Δ12-oleanene with a $CO_2H$ group attached to the C-17 position [5]. The signal centred at $\tau$ 6·65 for the C-3 hydrogen of the diol was a doublet indicating that there was only one OH group. The coupling constant (*J* 10 Hz) indicated the diaxial coupling between C-2–H and C-3–H. A signal at $\tau$ 5·94 (1H, *q*, *J* 10 Hz) for C-2–H showed the presence of two axial–axial couplings and one axial–equatorial coupling. From the above data the structure of the diol acid was thought to be 2α,3β-dihydroxyurs-12-en-28-oic acid. This compound was synthesised from asiatic acid (2α,3β,23α-trihydroxyurs-12-en-28-oic acid) and was identical with the resin diol acid.

The major component (*ca* 15%) of the petrol insoluble fraction of the resin showed a phase change at 235° and melted at 304–5°. The MW 488 (MS) and C,H analysis gave $C_{30}H_{48}O_5$, as the molecular formula of the compound. IR, PMR and MS data led to the conclusion that the compound is a $C_{17}$ carboxylic acid belonging either to the Δ12-ursene or Δ12-oleanene series [5]. The formation of an α-bromo-γ-lactone in very poor yield under forcing conditions indicated that the compound does not belong to the oleanene series [8]. Liberation of formaldehyde (identified as its dimedene derivative) when the compound was heated with copper showed the presence of a CHOH–C–$CH_2$OH group [9]. Formation of an acetonide derivative (with the Me ester of the compound) and the reaction with $HIO_4$ (with the free acid) indicated that at least two of the three OH groups were adjacent to each other. The triol acid was identified as asiatic acid [10] and was confirmed by comparison of the acid and its Me ester with authentic samples. 2α,3β-Dihydroxyurs-12-en-28-oic acid and asiatic acid have been isolated previously from Dipterocarpaceae resins but only as derivatives [5, 6, 7, 11]. This is the first time they have been isolated as the free acids.

Oxidation of asiatic acid at 0° using Jones' Reagent [12] gave a mixture of products. The MS of the major product exhibited a $M^+$ at *m/e* 486 indicating that only one OH group had been oxidised to a carbonyl group. The IR ($\nu_{max}$ 1722 $cm^{-1}$) and PMR $\tau$ 0·40 (1H, *s*, CHO) confirmed that the compound was obtained by the oxidation of the 23–OH group of asiatic acid. On the basis of these data and MS fragmentation, the oxidised product was identified as 2α,3β-dihydroxyurs-12-en-23-al-28-oic acid. This aldehyde when subjected to Barton's modification [13] of the Wolff–Kishner reduction gave 2α,3β-dihydroxyurs-12-en-28 oic acid. The reduced product was shown to be identical with 2α,3β-dihydroxyurs-12-en-28-oic acid isolated in this work. Oxidation of asiatic acid with $HIO_4$ consumed 1·2 mol and the IR spectrum of the compound had strong bands at 3420 and 1722 $cm^{-1}$. Esterification with diazomethane yielded a Me ester which was identical with the hemiacetal derivative of the Me ester reported by Rastogi and Singh [14]. Hence the $HIO_4$ oxidation product of asiatic acid was identified as the hemiacetal derivative of 2,3-seco-2,3-dioxo-23-hydroxyurs-12-en-28-oic acid.

The resins of *Dipterocarpus zeylanicus*, *Doona congestiflora* and *Doona macrophylla* were separated into neutral and acidic fractions and their components separated by column chromatography (Table 1).

The acidic fraction of the resin of *Doona congestiflora* on chromatography yielded a white solid (*ca* 0·4%) which was shown to be a terpenoid of MW 472 (MS). From the IR ($\nu_{max}$ 3400 $cm^{-1}$ and 1701 $cm^{-1}$) spectrum of the compound and the PMR signals at $\tau$ 6·38 (3H, *s*, $-CO_2Me$) for the Me ester, the compound was shown to be a monocarboxylic acid. The MS of the compound had intense peaks at *m/e* 248 (base), 203 and 133. The PMR spectrum of the compound showed the presence of an olefinic proton at $\tau$ 4·5 (1H, *m*, $W_{\frac{1}{2}} = 8$ Hz). These results indicated the compound to be a $C_{17}$ monocarboxylic acid belonging either to the Δ12-oleanene or Δ12-ursene series [5]. The PMR signals at $\tau$ 5·81 (1H, $W_{\frac{1}{2}} = 11$ Hz) appearing as a multiplet and at $\tau$ 6·31 (1H) appearing as a doublet (*J* 10 Hz) indicated it to be a vicinal dihydroxy compound [5]. These data in conjunction with the absence of PMR signals for secondary Me groups indicated the compound to be a dihydroxyolean-12-en-28-oic acid. The lack of more resin prevented further work on its structure. Asiatic acid (*ca* 4%) was isolated and identified from the resin.

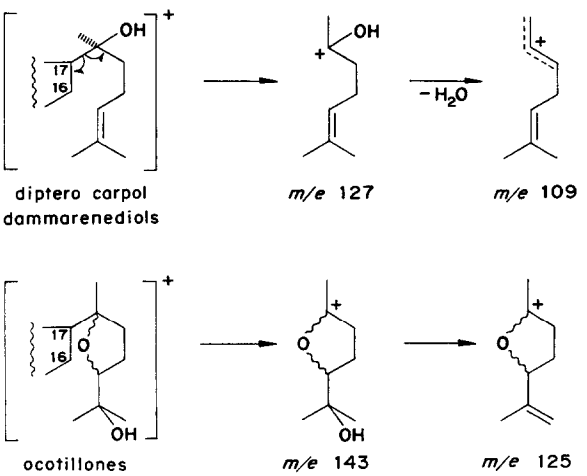
Table 1. Triterpenoids isolated from the *Dipterocarpaceae*

| Compounds | *Dipterocarpus Hispidus* Bark (%) | *Dipterocarpus Hispidus* Timber (%) | *Dipterocarpus Hispidus* Resin* (%) | *Dipterocarpus zeylanicus* Resin* (%) | *Doona congestiflora* Resin† (%) | *Doona macrophylla* Resin‡ (%) |
|---|---|---|---|---|---|---|
| Dipterocarpol | | 0·01 | 48·0 | 10·0 | 0·4 | |
| Ocotillone 20R | | | 0·05 | | | |
| Ocotillone 20S | | | 0·4 | | | |
| Dammarenediol 20R | | | | | 1·6 | |
| Dammarenediol 20S | 0·002 | | | | | |
| Ursolic acid | | | | | 0·3 | 3·0 |
| 2α,3β-Dihydroxyurs-12-en-28-oic acid | | | 0·2 | 0·4 | | 6·0 |
| Asiatic acid | | 0·02 | 15·0 | 22·0 | 4·0 | 8·4 |
| β-amyrin | | | | | 2·0 | |
| a Dihydroxyolean-12-en-28-oic acid | | | | | 0·4 | |
| Betulinic acid | 0·01 | | | | | |
| Triterpene acid | | | | | | 0·8 |
| Caryophyllene, Humulene, Alloaromadendrene | 0·4 | | | | | |

* Presence was shown by TLC examination only. † Preliminary investigations by Bisset *et al.* [2]. ‡ Preliminary investigations by Diaz, Ourisson and Bisset [4].

Although a partial chemical analysis of the resin of *Dipterocarpus hispidus* was achieved by Bisset *et al.* [2], the present study shows that dipterocarpol is present in the resin and also in the bark and timber of this species. Dipterocarpol, however, is present only in large quantities in the 2 *Dipterocarpus* species studied by us whereas the same compound is present only to a small extent in the 2 *Doona* species investigated. Ursolic acid is present only in the 2 *Doona* species. Asiatic acid which is present in both *Dipterocarpus* and *Doona* species could be of taxonomic significance. The isolation of betulinic acid from the family Dipterocarpaceae has not been previously reported.

The structure of dipterocarpol, dammarenediol 20R (3β,20α-Dihydroxydammar-23-ene), dammarenediol 20S, ocotillone 20R and ocotillone 20S were determined by chemical methods [15, 2] and subsequent work [16–18] showed that IR, PMR data were in agreement with initially assigned structures for these compounds. Additional information from MS for their structures has become available from the present study. It was significant that in these compounds the $M^+$ ions were not visible in the spectra. The ions with the largest *m/e* value recorded for dipterocarpol, dammarenediol 20R and dammarenediol 20S were those due to a loss of $H_2O$ from the $M^+$, whereas the ocotillones had ($M^+$-15) as the largest ions at the high end of the spectrum. The MS of the two ocotillones were identical and the two dammarenediols also had similar spectra. In all the compounds the base peak resulted from expulsion of the side chain. From the *m/e* values of the base peak it is possible to elucidate the nature of the side chains in these types of natural products. The fragmentation pattern is indicated in the Scheme 1.




Scheme 1.

## EXPERIMENTAL

Bark, timber and resin of *Dipterocarpus hispidus* were obtained from the Kanneliya forest near Udugama in the

south of Sri Lanka (Ceylon). The resin of *Dipterocarpus zeylanicus* and *Doona congestiflora* were collected from the forest at Kalawana–Morapitiya road. The resih of *Doona macrophylla* was provided by Dr. W. J. Meier.

The resins were dissolved in hot $CHCl_3$, filtered and separated from dried bark material and sand. The filtrate was concentrated and last traces of the solvent were removed under red press on a $H_2O$ bath. The bark and timber of *D. hispidus* were separated, chipped and powdered in a mill and the extractives obtained using petrol (bp 60–80°), $C_6H_6$ and MeOH. The solvents were removed under red press. Column chromatographic separations were effected on Si gel (30–70 mesh) or neutral alumina (Activity I). Si gel was used for analytical TLC separation. GLC analysis (FID. Apiezon L 2 m × 2 mm column) of the $CHCl_3$ sol of the resin of *Dipterocarpus hispidus* showed the presence of caryophyllene humulene and alloaromadendrin in the ratio 7:10:3 respectively.

*Resin of* Dipterocarpus hispidus. (a) *Isolation of dipterocarpol.* The resin (90 g) was separated into a petrol soluble (81 g) and an insoluble (9 g) fractions. The soluble fraction (80 g) on cooling deposited a white crystalline solid which was recrystallized from petrol to give dipterocarpol (8·1 g) as white shiny flakes, mp 135–136°, $[\alpha]_D^{26}$ +66·5° ($CHCl_3$) (lit, [15] 134–136°, $[\alpha]_D^{26}$ +66°), $R_f$ 0·74 ($CHCl_3$). MS *m/e* 424 (44%), 409 (1), 357 (27), 313 (9), 219 (10), 205 (40), 127 (22), 109 (100), 69 (63), 56 (22), 43 (37). It was shown to be identical with an authentic sample (mixed mp, IR, MS and TLC). The filtrate was further concentrated and on leaving it at 0° more crystals of dipterocarpol (9·6 g) were obtained. A further quantity of dipterocarpol (24·4 g) was obtained when the filtrate was concentrated and separated on a column of Si gel using $C_6H_6$–petrol (3:1). The overall yield of dipterocarpol obtained was 48%. (b) *Isolation of ocotillone* 20*S*. Elution of the Si gel column with $C_6H_6$ gave a mixture (1·6 g). This mixture was chromatographed on a column of neutral alumina (45 g). Elution with $Et_2O$–petrol (7:93) gave a white solid which on crystallisation from petrol gave ocotillone 20S (35 mg, 0·043%) as white needles mp 164–165°, $[\alpha]_D^{26}$ +59° ($CHCl_3$) (lit [2] 165°, $[\alpha]_D^{26}$ +63°), $R_f$ 0·55 ($CHCl_3$). MS *m/e* 443 (6%), 399 (40), 381 (13), 358 (2), 315 (2), 257 (3), 246 (4), 205 (15), 143 (100), 125 (25). It was shown to be identical with an authentic sample (mixed mp, IR, MS, rotation and TLC). (c) *Isolation of ocotillone* 20*R*. The Si gel column when eluted with $Et_2O$–petrol (9:91) gave a white solid which on crystallization from petrol gave ocotillone 20R (40 mg, 0·05%) as white needles mp 184–186°, $[\alpha]_D^{26}$ +48·5° ($CHCl_3$) (lit [2], 186°, $[\alpha]_D^{26}$ +50°), $R_f$ 0·55 ($CHCl_3$). The MS was identical with that obtained for ocotillone 20S. The compound was shown to be identical with an authentic sample (mixed mp, IR, MS, rotation and TLC). (d) *Isolation of 2α,3β-dihydroxyurs-12-en-28-oic acid.* The petrol insoluble fraction of the resin (90 g) was chromatographed on a column of Si gel. Elution with $CHCl_3$–MeOH (98:2) gave a white solid which on crystallisation from MeOH yielded 2α,3β-dihydroxyurs-12-en-28-oic acid as a white powder (115 mg, 0·13%), mp 253–254°, $[\alpha]_D^{26}$ +44·2° ($C_5H_5N$) (lit [7] 243–245, $[\alpha]_D^{26}$ +42·1°), $R_f$ 0·43 [$CHCl_3$–MeOH (9:1)], PMR τ ($C_5D_5N$, 100 MHz) 4·56 (1H, *m*, $W_{\frac{1}{2}}$ = 8 Hz, 12-H), 5·94 (1H, *q*, *J* 11 11 Hz, 2-H), 6·65 (1H, *d*, *J* 9 Hz, 3-H), 7·66–8·62 (satd($CH_2$), 8·00, 8·76, 8·96, 8·99, 9·01 × 2, 9·04 (7 × 3H, *s*, Me-groups). MS *m/e* 472 (2%), 454 (3%), 426 (3), 409 (4), 248 (100), 219 (14), 203 (60), 189 (12), 133 (48). It was shown to be identical with an authentic sample of 2α,3β-dihydroxyurs-12-en-28-oic acid (mixed mp, IR, rotation and TLC) prepared from asiatic acid. Acetylation with $(Ac)_2O$ and $C_5H_5N$ at room temp for 24 hr and usual work up gave 2α,3β-diacetoxyurs-12-en-28-oic acid mp 218°, (from petrol), $[\alpha]_D^{26}$ +25·6° ($CHCl_3$), $R_f$ 0·32 ($CHCl_3$). [Found $M^+$ (MS) 556. $C_{34}H_{52}O_6$ requires $M^+$ 556]. IR $\nu_{max}$ (nujol) 1740, 1695, $cm^{-1}$. PMR τ ($CDCl_3$, 100 MHz) 4·76 (1H, *m*, $W_{\frac{1}{2}}$ = 8 Hz, 12-H), 4·95 (1H, *m*, $W_{\frac{1}{2}}$ = 16 Hz, 2-H), 5·26 (1H, *d*, *J* 11 Hz, 3-H), 7·95 (3H, *s*, –OCOMe), 8·02 (3H, *s*, –OCOMe), 7·8–8·64 (satd–$CH_2$), 9·74, 8·92 × 2, 9·10 × 3, 9·23 (7 × 3H, *s*, –Me groups). MS *m/e* 556 (3), 541 (2), 510 (5), 436 (10), 421 (5), 248 (100), 235 (13), 219 (15), 203 (90), 189 (42), 173 (20).

(e) *Isolation of asiatic acid.* Elution of the Si gel column with $CHCl_3$–MeOH (95:5) gave a white solid which on repeated crystallization from MeOH yielded asiatic acid (8·1 g, 15%) as a white powder, mp 303–305°, $[\alpha]_D^{26}$ +52° ($C_5H_5N$) (lit, [19] 300–305°, $[\alpha]_D^{26}$ +53°). $R_f$ 0·25 [$CHCl_3$:MeOH (9:1)], PMR τ ($CD_3OD$, 100 MHz) 4·77 (1H, *m*, 12-H), 6·31 (1H, *m*, $W_{\frac{1}{2}}$ = 2·5 Hz, 2-H), 6·48 (1H, *d*, *J* 10 Hz, 3-H), 7·70–8·81 (satd $CH_2$), 8·87, 8·96, 9·04, 9·02, 9·15 and 9·30 (6 × 3H, *s*, –Me groups). MS *m/e* 488 (15%), 470 (9), 452 (15), 425 (16), 411 (9), 393 (9), 368 (15), 301 (14), 248 (100), 203 (60), 133 (48). The Me ester was prepared from 0·1 g in $Et_2O$ (50 ml) and MeOH (1 ml) and treatment with excess $CH_2N_2$. Usual work up gave Me asiatate (90 mg) as white needles (from MeOH) mp 216–217°, $[\alpha]_D^{26}$ +54·8° ($CHCl_3$) (lit, [19] 212–220°, $[\alpha]_D^{26}$ +54·5°), $R_f$ 0·45 [$CHCl_3$:MeOH (9:1)], PMR τ ($CDCl_3$, 100 MHz), 4·76 (1H, *m*, $W_{\frac{1}{2}}$ = 7 Hz, 12-H), 5·96 (1H, *m*, $W_{\frac{1}{2}}$ = 12 Hz, 2-H), 6·42 (3H, *s*, $-CO_2Me$), 6·58 (3H, *s*, 23-H and 3-H), 7·1–8·84 (satd $CH_2$), 8·93, 9·06, 9·08, 9·12, 9·20, 9·27 (6 × 3H, *s*, –Me groups). MS *m/e* 502 (4%), 442 (5), 262 (100), 249 (20), 233 (6), 203 (96), 191 (15), 189 (24), 133 (50), 121 (12), 119 (20). The acid (50 mg) was acetylated using $(Ac)_2O$ (0·5 ml), and $C_5H_5N$ (3 ml) at room temp. Usual work up and crystallization from MeOH gave 2α,3β,23α-triacetoxyurs-12-en-28-oic acid (35 mg) as a white powder mp 161–162°, $[\alpha]_D^{26}$ +21° (MeOH), $R_f$ 0·35 ($CHCl_3$). IR $\nu_{max}$ (nujol) 1743, 1695 $cm^{-1}$. PMR τ ($CDCl_3$, 100 MHz) 4·75 (1H, *t*, *J* 7 Hz, 12-H), 4·81 (1H, *m*, $W_{\frac{1}{2}}$ = 12 Hz, 2-H), 4·89 (1H, *d*, *J* 7 Hz, 3-H), 6·29 (2H, *q*, *J* 2·8, 12 Hz, 23-$CH_2$), 7·92 (3H, *s*, –OCOMe), 8·00 (3H, *s*, –OCOMe), 8·02 (3H, *s*, –OCOMe), 8·02–8·81 (satd $CH_2$), 8·90, 8·93, 9·05, 9·13, 9·18, 9·23 (6 × 3H, *s*, –Me groups).

*Addition of bromine to asiatic acid and conversion to the α-bromo-γ-lactone.* 3% $Br_2$ in HOAc (3 ml) was added dropwise to a soln of asiatic acid (50 mg), NaOAc (0·2 g), HOAc (9 ml) and $H_2O$ (1 ml). The mixture was shaken for 15 min and was left 18 hr at room temp. The reaction mixture was poured into $H_2O$ containing $Na_2S_2O_3$. The solid which separated was extracted with $Et_2O$ and was washed with a soln of $K_2CO_3$ (5%) and then with $H_2O$. The crude product (45 mg) was chromatographed on a column of Si gel. Elution with $CHCl_3$–$C_6H_6$ (95:5) gave a white solid which on crystallization from MeOH yielded 12α-bromo-13γ-lactone of asiatic acid (8 mg) as a white powder mp 179–180°, $[\alpha]_D^{26}$ +99·6° ($CHCl_3$), $R_f$ 0·49 [$CHCl_3$:MeOH (9:1)]. IR $\nu_{max}$ (nujol) 3400, 1771 $cm^{-1}$. *Oxidation of asiatic acid with periodic acid.* Asiatic acid (50 mg) in MeOH (10 ml) was treated with $HIO_4$ (20 mg) and the reaction mixture was left 18 hr. The reaction mixture was diluted with $H_2O$ and then extracted with $Et_2O$. The residue obtained on evaporation of the solvent was recrystallized from MeOH to give the hemiacetal derivative of 2,3-seco-2,3-dioxo-23-hydroxyurs-12-en-28-oic acid (45 mg), mp 145–146°, $[\alpha]_D^{26}$ +137° ($CHCl_3$), $R_f$ 0·80 [$CHCl_3$–MeOH (9:1)] [Found $M^+$ (MS) 468. $C_{30}H_{44}O_4$ requires $M^+$ 468]. IR $\nu_{max}$ (KBr) 3420, 2928, 1722, 1694 $cm^{-1}$. MS *m/e* 468 (6%), 424 (3), 413 (4), 355 (3), 309 (3), 248 (100), 225 (26), 203 (37), 133 (41), 119 (29), 105 (38) 95 (40). The hemiacetal derivative was esterified with $CH_2N_2$ to give the Me-ester

mp 114–5°, $[\alpha]_D^{26}$ +115° (lit, [14] 115°). Another expt revealed that one mol of asiatic acid had reacted with 1·2 mol of $HIO_4$.

*Reaction of asiatic acid with precipitated copper.* Asiatic acid (100 mg) was heated with freshly pptd Cu at 300° for 2 hr. Evolved gas was passed through aq. (satd) soln of dimedone. The ppt formed was filtered and washed with $H_2O$. Crystallization from MeOH yielded the HCHO dimedone derivative as white needles (6 mg), mp 188–189° (lit, [9] 188–189°). It was shown to be identical with an authentic sample of HCHO dimedone derivative (mmp, and TLC). *Acetonide of Me asiatate.* Me asiatate (25 mg) was suspended in dry $Me_2CO$ (3 ml) and $Me_2CO$ saturated with dry HCl (0·5 ml) was added. The mixture was shaken for 10 min and was left 18 hr. Solvent was evaporated under red pres and the residue washed with $NaHCO_3$ (5%) soln and then with $H_2O$. The crude product was chromatographed on a Si gel column and elution with $CHCl_3$–$C_6H_6$ (95:5) gave a white solid which on crystallization from MeOH yielded the acetonide of methyl asiatate (16 mg) as white needles, mp 212–214°, $[\alpha]_D^{26}$ +44·4° ($CHCl_3$) (lit, [10] 213–214°, $[\alpha]_D^{26}$ +45·5°), IR $\nu_{max}$ (nujol) 3400, 1733 $cm^{-1}$. *Oxidation of asiatic acid with Jones' Reagent.* Asiatic acid (100 mg) in $Me_2CO$ was cooled at 0° and Jones' reagent [12] was added. The mixture was shaken for 5 min and was left 18 hr at 5°. The reaction mixture was diluted with $H_2O$ and was extracted with $Et_2O$. The crude solid (95 mg) was separated on a column of Si gel and elution with $CHCl_3$. The white solid on crystallization from MeOH gave 2α,3β-dihydroxyures-12-en-23-al-28-oic acid (42 mg), mp 239–40°, $[\alpha]_D^{26}$ +18·3° ($CHCl_3$), $R_f$ 0·43 [$CHCl_3$:MeOH (9:1)]. [Found $M^+$ (MS) 486. $C_{30}H_{46}O_5$ requires $M^+$ 486], IR $\nu_{max}$ (KBr) 3430, 2915, 2860, 1722, 1696 $cm^{-1}$. PMR τ ($C_5D_5N$, 100 MHz) 0·40 (1H, *s*, 23-CHO), 4·54 (1H, *m*, 12-H), 5·99 (1H, *d*, *J* 10 Hz, 3-H), 6·36 (1H, *m*, $W_{\frac{1}{2}}$ = 15 Hz, 2-H), 7·62–8·54 (satd-$CH_2$), 8·59, 8·79, 8·99 × 2, 9·03 × 2 (6 × 3H, *s*, –Me groups). MS *m/e* 486 (2%), 471 (1), 468 (2), 439 (5), 248 (100), 235 (14), 203 (58), 133 (40). *Modified Wolff-Kishner reduction of 2α,3β-dihydroxyurs-12-en-23-al-28-oic acid.* The compound (20 mg) in freshly distilled diethylene glycol (8 ml) and freshly prepared anhydrous hydrazine (0·5 ml) and Na (0·2 g) were heated under reflux at 130° for 3 hr. The temp of the reaction mixture was increased by removal of excess hydrazine and temp was maintained at 180° for 2 hr. The reaction mixture was cooled, diluted with $H_2O$ and extracted with $Et_2O$. The crude product was chromatographed on a Si gel column gel and elution with $CHCl_3$–MeOH (98:2) gave a solid which was crystallized from MeOH to give 2α,3β-dihydroxyurs-12-en-28-oic acid (10 mg) as a white powder mp 253–254°, $[\alpha]_D^{26}$ +45° ($C_5H_5N$). The product was shown to be identical with the 2α,3β-dihydroxyurs-12-en-28-oic acid isolated in this study.

*Resin of* Dipterocarpus zcylanicus. The hot petrol insoluble fraction (4 g) of the resin was chromatographed on a column of Si gel. Elution with $C_6H_6$–petrol (3:1) gave dipterocarpol (1 g, 10%) mp 135–136°. Another portion (5 g) when chromatographed on Si gel and eluted with $CHCl_3$–MeOH (98:2) gave a white solid which was crystallized from MeOH to give 2α,3β-dihydroxyurs-12-en-28-oic acid (26 mg, 0·4%), mp 242–243°. Further elution of the column with $CHCl_3$–MeOH (95:5) yielded asiatic acid (1·1 g, 22%), mp 299–300°.

*Resin of* Doona congestiflora. $CHCl_3$ and $Me_2CO$ soluble fraction (15 g) of the resin was repeatedly separated on Si gel columns to give β-amyrin (105 mg, 2%), mp 198–199°; dipterocarpol (18 mg, 0·4%) mp 134–135° and dammarenediol 20R (80 mg, 1·6%) as white shiny crystals (petrol) mp 141–142°, $[\alpha]_D^{26}$ +28·1° (lit, [15] 142°, $[\alpha]_D^{26}$ +27°), $R_f$ 0·23, [$C_6H_6$–$CHCl_3$, (1:1)], Dammarenediol 20R (was acetylated ($Ac_2O$–$C_5H_5N$ at room temp) to give the acetate mp 145–146°, $[\alpha]_D^{26}$ +41·2° ($CHCl_3$) (lit, [20] 145–147°, $[\alpha]_D^{26}$ +40°), $R_f$ 0·70 [$C_6H_6$–$CHCl_3$ (1:1)]. MS of diol *m/e* 426 (22%), 411 (3), 401 (8), 383 (11), 361 (6), 357 (9), 343 (6), 315 (6), 300 (9), 207 (54), 191 (45), 189 (39), 161 (36), 143 (96), 135 (93), 127 (51), 121 (81), 109 (100), 107 (90), 95 (90). Another portion of the mixture (1·2 g) obtained from the $CHCl_3$–$Me_2CO$ soluble fraction of the resin was chromatographed on a column of neutral alumina. Elution with $CHCl_3$–EtOAc (95:5) gave a white solid which on crystallization from EtOH afforded ursolic acid (55 mg, 0·3%) as white crystals mp 282°, $[\alpha]_D^{26}$ +66·2° ($C_5H_5N$) (lit, [21] 283–284°, $[\alpha]_D^{26}$ +65·9°), $R_f$ 0·20 [$CHCl_3$–EtOH (98:2)]. It was shown to be identical with an authentic sample (mixed mp, acetate, IR, rotation and TLC). After separation of ursolic acid the column was eluted with $CHCl_3$–EtOAc (92:8) to give a white solid which on crystallization from MeOH gave a dihydroxyolean-12-en-28-oic acid (55 mg, 0·4%), mp 293–295°, $[\alpha]_D^{26}$ +81·3° (MeOH), $R_f$ 0·20 ($CHCl_3$–MeOH 98:2). [Found $M^+$ (MS) 472. $C_{30}H_{48}O_4$ requires $M^+$ 472]. IR $\nu_{max}$ (KBr) 3400, 2940, 2875, 1701, 1490, 1380, 1255, 1235, 1190, 1090, 1050, 1005 and 965 $cm^{-1}$. PMR τ ($C_5D_5N$, 100 MHz) 4·52 (1H, *m*, $W_{\frac{1}{2}}$ = 8 Hz, 12-H); 5·81 (1H, *m*, $W_{\frac{1}{2}}$ = 11 Hz, 2-H); 6·31 (1H, *d*, *J* 10 Hz, 3-H); 7·50–8·62 (satd –$CH_2$); 8·75, 8·81, 8·96 × 2, 8·99, 9·02 × 2 (7 × 3H, *s*, –Me groups). MS *m/e* 472 (2%), 454 (3), 436 (3), 425 (3), 395 (2), 248 (100), 203 (50), 175 (22), 133 (35). The acid was esterified with $CH_2N_2$ and the Me ester crystallized from MeOH to give white crystals mp 251–252°, $[\alpha]_D^{26}$ +79·2° ($CHCl_3$), $R_f$ 0·70, [$CHCl_3$–MeOH (95:5)]. IR $\nu_{max}$ (KBr) 3320, 2936, 1728, 1460, 1431, 1395, 1370, 1350, 1309, 1275, 1206, 1140, 1138, 1110, 1088, 1046, 1001, 956, 910, 867, 831 and 810 $cm^{-1}$. PMR τ ($CDCl_3$, 100 MHz) 4·71 (1H, *m*, $W_{\frac{1}{2}}$ = 13 Hz, 12-H), 6·38 (3H, *s*, $-CO_2Me$), 6·25 (1H, *m*, partly obscured by $-CO_2Me$ signal 2-H), 6·26 (1H, *d*, *J* 8 Hz, 3-H), 7·95–8·10 (satd –$CH_2$), 8·90, 9·01 × 2, 9·00 × 2, 9·15, 9·22 (7 × 3H, *s*, Me groups). The $CHCl_3$ and $Me_2CO$ soluble fraction (15 g) of the resin when repeatedly separated on Si gel columns gave asiatic acid (45 mg, 4%) as a white powder, mp 303–304° $[\alpha]_D^{26}$ +53·4° ($C_5H_5N$). It was identical with an authentic sample.

*Resin of* Doona macrophylla. Dried resin powder (5 g) was chromatographed on a column of Si gel. Elution with $C_6H_6$ separated less polar compounds. Continued elution with $CHCl_3$ gave a white solid which was crystallized from EtOH–$H_2O$ to give a triterpene acid (43 mg, 0·8%) as a white powder mp 200–210°. There were no UV absorptions above 225 nm. IR $\nu_{max}$ (nujol) 3445, 1695, 1320, 1280, 1240, 1220, 1120, 1080, 1060, 1045, 980, 845, 815, 770, 760, 745 and 670 $cm^{-1}$. PMR τ ($CDCl_3$, 60 MHz) 4·45 (1H, *s*, –C=CH), 7·75 (2H, *m*, $-CH_2$–C=O), 8·00–9·1 (satd $-CH_2$ and –Me groups). Found $M^+$ (MS) 468. $C_{30}H_{44}O_4$ requires $M^+$ 468. MS *m/e* 468 (4%), 454 (12), 426 (4), 248 (100), 235 (11), 234 (4), 205 (16), 203 (46), 187 (6), 133 (26). Continued elution with $CHCl_3$–MeOH (99:1) gave ursolic acid (16 mg, 3%) mp 282°. Further elution with $CHCl_3$–MeOH (97:3) yielded 2α,3β-dihydroxyurs-12-en-28-oic acid (32 mg, 6%) mp 242–3°. Elution was continued with $CHCl_3$–MeOH (95:5) to give asiatic acid (42 mg, 8·4%) mp 297–300°.

*Bark of Dipterocarpus hispidus.* (a) *Isolation of betulinic acid.* The $C_6H_6$ extract (3·5 g) of the powdered bark (1·35 kg) gave a petrol insoluble solid (1·8 g). The solid (1 g) was chromatographed on a column of Si gel and elution with $C_6H_6$–$CHCl_3$ (3:1) gave a white solid which on crystallization from MeOH yielded betulinic acid (95 mg, 0·014%), mp 299–300° $[\alpha]_D^{26}$ +13° ($CHCl_3$) (lit, [22] 306–310°, $[\alpha]_D^{26}$ +9°), $R_f$ 0·70 ($CHCl_3$–MeOH, 9:1). It was shown to be identical

with an authentic sample (m mp IR, rotation and TLC). (b) *Isolation of dammarenediol 20S.* Powdered bark (1·35 kg) gave a petrol and $C_6H_6$ insoluble and MeOH soluble fraction (91 g). The MeOH extract (50 g) was re-extracted with $CHCl_3$ in a Soxhlet extractor for 4 days and the extract (1·4 g) was then chromatographed on a Si gel column. Elution with $C_6H_6$–petrol (4:1) yielded a white solid which was recrystallized from petrol to give dammarenediol 20S (22 mg, 0·002%) as white needles, mp 131–132°, $[\alpha]_D^{26}$ +30° ($CHCl_3$) (lit. [20] 133–135°, $[\alpha]_D^{26}$ +35°), $R_f$ 0·23 ($C_6H_6$–$CHCl_3$ 1:1). MS *m/e* 426 (31%), 411 (2), 401 (0·2), 383 (1), 361 (2), 357 (7), 343 (4), 315 (4), 300 (4), 207 (57), 191 (43), 189 (40), 161 (17), 143 (2), 135 (43), 127 (31), 121 (34), 109 (100), 107 (43), 95 (66). The compound was shown to be identical with an authentic sample (mmp, acetate, IR, rotation and TLC).

*Timber of* Dipterocarpus hispidus. Powdered timber (11·5 kg) gave 161 g of $C_6H_6$ soluble and 390 g of MeOH soluble materials. The MeOH extract by TLC was similar to that of the resin and was re-extracted with $Et_2O$ in a Soxhlet extractor. The $Et_2O$ soluble fraction yielded 15 g of a brown solid which was chromatographed on a Si gel column. Elution with $C_6H_6$–$CHCl_3$(4:1) gave a white solid which on crystallization from petrol gave dipterocarpol (90 mg, 0·11%) mp 133–135°. Further elution with $CHCl_3$–MeOH (95:5) yielded asiatic acid (110 mg, 0·014%) mp 302–304°.

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