Chemical Investigation of Ceylonese Plants. Part 20.† Extractives of *Mesua myrtifolia*. Isolation and Structure of a New Triterpene Hydroxy-acid, Myrtifolic Acid

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From the bark extractives of *Mesua myrtifolia* (a Malaysian species) simiarenone, simiarenol, taraxerol, betulinic acid, and a new triterpene acid, myrtifolic acid, have been isolated. The latter has been correlated with bauerene and identified as 3α-hydroxybauer-7-en-28-oic acid. From the timber extractives myrtifolic acid, oleanolic acid, and jacareubin have been obtained.

In Part 15,[1] the need to examine the extractives of some Malaysian species was suggested. *Mesua myrtifolia*, a Malaysian species of the sub-family Calophylloideae has been investigated and the present paper reports our results. Studies on only three *Mesua* species [*M. ferrea* L.,[2] *M. thwaitesii* Thw.,[3] and *M. ferrea* (form *M. salicina*) Pl. and Tr.[4]] have been reported to date.

Bark Extractives.—The light petroleum extract of the bark was taken up in diethyl ether and washed with cold sodium carbonate and sodium hydroxide solution to remove acidic and phenolic material, respectively. The neutral material from the ether solution was separated

† Part 19. V. Kumar, S. Ramachandran, and M. U. S. Sultanbawa, *Phytochemistry*, in the press.

[1] S. P. Gunasekera and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1975, 1539.

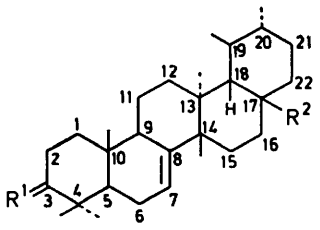
[2] (*a*) T. R. Govindachari, B. R. Pai, P. S. Subramaniam, U. R. Rao, and N. Muthukumaraswamy, *Tetrahedron*, 1967, **23**, 243; (*b*) Y. L. Chow and H. H. Quon, *Phytochemistry*, 1967, **7**, 1871; (*c*) D. P. Chakraborty and D. Chatterjee, *J. Org. Chem.*, 1969, **34**, 3784.

[3] W. M. Bandaranayake, S. Selliah, M. U. S. Sultanbawa, and D. E. Games, *Phytochemistry*, 1975, **14**, 265.

[4] S. P. Gunasekera, S. Ramachandran, S. S. Selliah, and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1975, 2447.

on a silica gel column with solvents of increasing polarity to give β-sitosterol and four terpenoid compounds. All these were obtained pure by crystallisation and characterised as simiarenon,[5] simiarenole,[5] taraxerol,[6] and betulinic acid[7] from their m.p.s, specific rotations, and i.r. spectra. The structures were confirmed by comparison with authentic samples (mixed m.p.s, i.r. spectra, and t.l.c.).

The sodium hydroxide-soluble fraction on separation on a silica gel column (chloroform) gave a white crystalline



(1)

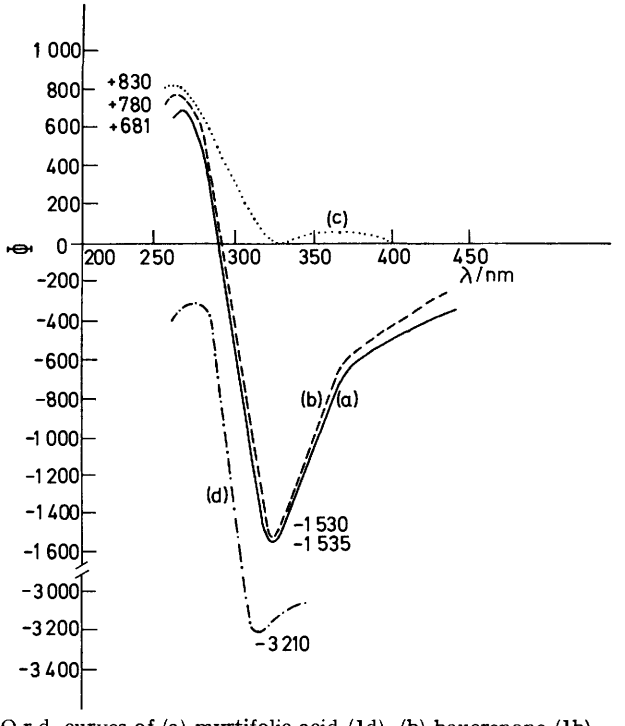
a; R^1 = H_2; R^2 = Me
b; R^1 = O; R^2 = Me
c; R^1 = β-OH,H; R^2 = Me
d; R^1 = α-OH,H; R^2 = CO_2H
e; R^1 = α-OH,H; R^2 = CO_2Me
f; R^1 = O; R^2 = CO_2H
g; R^1 = α-OH,H; R^2 = CH_2·OH
h; R^1 = O; R^2 = CHO

compound, m.p. 259—260°, named myrtifolic acid. This responded to a Liebermann–Burchard test for a terpenoid, and high resolution mass measurement gave the molecular formula $C_{30}H_{48}O_3$. The i.r. spectrum (Nujol) showed strong absorptions at 3 550 (OH) and 1 700 cm^{-1} (C=O of an acid). The ready methylation of the compound with diazomethane and the shift of C=O absorption of the product, methyl myrtifolate, to 1 726 cm^{-1} confirmed the presence of a carboxy-group. The n.m.r. spectrum of methyl myrtifolate (1e) showed an olefinic one-proton multiplet at τ 4.62 (1 H). A one-proton multiplet at τ 6.72 ($W_{\frac{1}{2}}$ 2 Hz) was attributed to C*H*·OH. The low $W_{\frac{1}{2}}$ value indicated an axial orientation for the hydroxy-group. The ester methyl signal appeared at τ 6.60 as a singlet, and singlets at τ 8.84, 9.00, 9.02, 9.05, and 9.13 were attributed to one tertiary allylic and four tertiary methyl groups, respectively. Further two doublets at τ 9.13 (J 6 Hz) and 9.23 (J 5 Hz) indicated the presence of two secondary methyl groups.[8]

As all the polyoxygenated naturally occurring triterpenoids isolated [9,10] to date contain an oxygen function at position 3, the hydroxy-group was tentatively placed at that position.

Reduction of methyl myrtifolate (1e) with lithium aluminium hydride gave the diol myrtifolol (1 g), M^+ 442, $C_{30}H_{50}O_2$, $\nu_{max.}$ (KBr) 3 300s cm^{-1} (OH). The disappearance of the carbonyl absorption indicated that the ester group was reduced. Oxidation of myrtifolol (1g) with chromic acid in aqueous acetic acid gave two products. These were separated on a silica gel plate into myrtifonic acid (1f), identical with that obtained by the oxidation of myrtifolic acid with chromic acid in pyridine (see below), and a less polar compound, $\nu_{max.}$ 1 714 (six-membered ring C:O) and 1 722 cm^{-1} (CH:O), identified as myrtifonal (1h).

The mass spectral fragmentation patterns [11] of myrtifolic acid and its derivatives were similar to those reported for bauerenone (1b) and bauerenol (1c). The presence of the base peak at *m/e* 245 (B) in the spectrum of myrtifonic acid (1f) further indicated that this compound has the bauerenone skeleton. Fernenone, arborenone, and multiflorenone skeletons show mass spectral fragmentations similar to that of bauerenone (1b), but their base peaks appear at *m/e* 257 (fernenone and arborenone) and at *m/e* 218 (multiflorenone).[12] As the n.m.r. spectrum of methyl myrtifolate showed the presence of two secondary methyl groups, the possibility of



O.r.d. curves of (a) myrtifolic acid (1d), (b) bauerenone (1b), (c) arborenone, and (d) fernenone

the compound having the multiflorenone skeleton, which contains no secondary methyl groups, was eliminated.

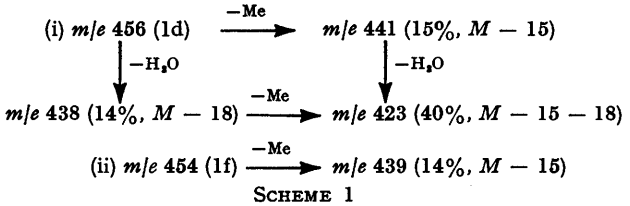
Huang-Minlon reduction [13] of myrtifonal (1h) gave a

[5] R. T. Alpin, H. R. Arthur, and W. H. Hui, *J. Chem. Soc.* (*C*), 1966, 1251.
[6] S. Burrows and J. C. E. Simpson, *J. Chem. Soc.*, 1938, 2042.
[7] A. Robertson, G. Soliman, and E. C. Owen, *J. Chem. Soc.*, 1939, 1237.
[8] L. M. Jackman and S. Sternhell, 'Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, London, 1969.
[9] B. Basa and R. P. Rastogi, *Phytochemistry*, 1967, **7**, 1249.
[10] S. K. Agarwal and R. P. Rastogi, *Phytochemistry*, 1974, **13**, 2623.
[11] H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688.
[12] S. Sengupta and H. N. Khastgir, *Tetrahedron*, 1963, **19**, 123.
[13] Huang Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

hydrocarbon (1a), $C_{30}H_{50}$ (M^+ 410), identical with authentic bauerene (1a) prepared by reduction of bauerenone (1b). Thus myrtifolic acid has the bauerene skeleton.

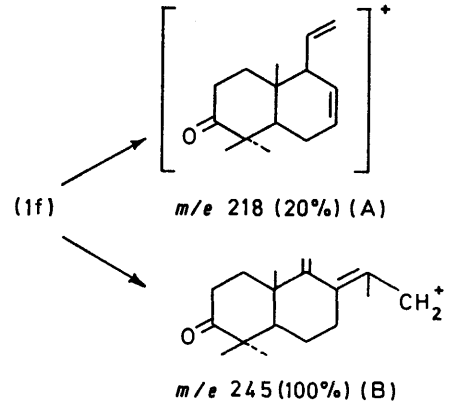
Oxidation of myrtifolic acid (1d) with chromic acid in pyridine gave myrtifonic acid (1f) (M^+ 454), $C_{30}H_{46}O_3$, $\nu_{max.}$ ($CHCl_3$) 1 695 (acid C:O) and 1 710 cm^{-1} (six-membered ring C:O). The o.r.d. curve of this compound showed a negative Cotton effect, $[\phi]_{320}$ −1 530tr, $[\phi]_{265}$ +681 pk, and was similar to the o.r.d. curve of bauerenone [14] (see Figure), which also had a negative Cotton effect, $[\phi]_{320}$ −1 535tr, $[\phi]_{260}$ +780pk, but distinct from those of arborenone [15] and fernenone.[16] This further supported the bauerenone (1a) skeleton for myrtifonic acid.[17] In addition, it indicated the presence of an oxo-group at C-3, confirming the oxygenation at C-3 of myrtifolic acid.

The mass spectra of myrtifolic acid and its derivatives show the ready removal of methyl group from the molecular ion (Scheme 1), indicating the presence of an allylic



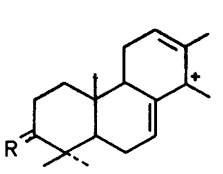
SCHEME 1

methyl group. This was supported by the presence of an allylic methyl signal in the n.m.r. spectrum of methyl

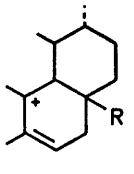


SCHEME 2

myrtifolate. The formation of fragments *m/e* 218 (A) and 245 (B) (Scheme 2) from myrtifonic acid (1f) revealed the absence of a carboxy-group in ring A or B. The axial methyl group at C-13 is sterically hindered as rings D and E are *cis*-fused in the bauerene skeleton.[18] The high reactivity of these compounds towards methylation, reduction with lithium aluminium hydride, oxidation with chromic acid, and Huang-Minlon reduction clearly indicated that the carboxy-group is not hindered. This eliminated the possibility of the carboxy-group being at C-13. Further the fragment (C) from compounds (1d—g) confirmed the absence of a carboxy-group in rings A, B, and C of the basic skeleton. The



(C)



(D)

presence of an intense peak due to the ion (D) in the spectra of compounds (1d—g) confirmed the presence of oxygenation at C-17, C-19, or C-20. As the compound containd two secondary methyl groups (n.m.r. spectrum) positions C-19 and C-20 could be eliminated, confirming the oxygenation at C-17.

The above data establish that myrtifolic acid (1d) is 3α-hydroxybauer-7-en-28-oic acid (IVd).

Bauerenol (1c) has been isolated previously from the barks of *Acronchia bauereri* [17] and *Gelonium multiflorum*,[12] both belonging to the family Rubiaceae.

Timber Extractives.—The alkali washing of the light petroleum extract of the timber gave traces of acidic and phenolic fractions. The acidic fraction was separated on a silica gel plate into myrtifolic acid (1d) and oleanolic acid.[19]

The methanol extract, after extraction with chloroform, was extracted with ethyl acetate. The ethyl acetate extract was chromatographed and a yellow compound was isolated. U.v. and i.r. spectra suggested that this was a xanthone, and it was identified as jacareubin [20] (XIII) by comparison with an authentic sample.

In the presence of its triterpenoid constituents and that of the prenylated xanthone (jacareubin), *M. myrtifolia* showed a greater resemblance to the genus *Kayea* than to the genus *Mesua*. The constituents so far reported from the latter genus are only simple xanthones. The occurrence of jacareubin in this genus again raises the question of its use as a chemotaxonomic marker for the genus *Calophyllum*, as it has also been reported to occur in the genera *Kielmeyera* [21] and *Pentadesma*.[22]

EXPERIMENTAL

U.v. and i.r. spectral data were recorded with a Unicam SP 8000B and a Perkin-Elmer 257 grating spectrophotometer respectively. Mass spectral data were obtained from the Universities of Strathclyde and Pennsylvania and the Australian National University. The n.m.r. data were

[14] C. Djerassi, 'Optical Rotatory Dispersion Applications in Organic Chemistry,' McGraw-Hill, New York, 1960, p. 92.
[15] O. Kennard, L. R. de Sanseverino, H. Vorbruggen, and C. Djerassi, *Tetrahedron Letters*, 1965, 3433.
[16] S. R. Kundu, A. Chaterjee, and A. S. Rao, *Tetrahedron Letters*, 1966, 1043.
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[22] W. D. Ollis, K. Sivapalan, and M. U. S. Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1973, **29**, 127.

obtained from the Tropical Products Institute, London. Optical rotations were determined with a Bellingham and Stanley polarimeter. M.p.s were determined with a Kofler hot-stage apparatus. R_F Values refer to t.l.c. on silica gel G (thickness 0.25 mm). Merck silica gel (30—70 mesh) was used for column chromatography and Merck silica gel $PF_{254-366}$ was used for preparative t.l.c. Light petroleum refers to the fraction, b.p. 60—80 °C.

The plant material (Herb. No. S 32096) was obtained from the Conservator of Forests, Kuching, Sarawak, Malaysia. The bark and timber were chipped and powdered in a mill. The powdered bark (5.5 kg) and powdered timber (6.5 kg) were extracted successively with hot light petroleum and hot methanol. The bark extract on concentration furnished the light petroleum-soluble fraction as a gum (A) (38.3 g, 0.67%) and the methanol-soluble fraction as a brown mass (B) (295 g 5.4%). Similarly the timber gave a light petroleum extract (2.1 g, 0.03%) and a methanol extract (201 g, 3.0%).

Light Petroleum Extract of the Bark.—The light petroleum extract of the bark (15 g) in diethyl ether (1.5 l) was washed with cold 5% sodium carbonate solution. The carbonate-soluble fraction was acidified with dilute hydrochloric acid and extracted with diethyl ether. Evaporation yielded a reddish brown solid (0.150 g, 0.007%). The organic layer was then washed with 5% sodium hydroxide. Work-up of the phenolic fraction produced a brown solid (0.101 g, 0.000 4%). The neutral fraction on evaporation furnished a pale brown gum (14.5 g, 0.57%).

Isolation of Simiarenone.—The neutral fraction (2 g) was chromatographed on a column of silica gel (80 g). Elution with benzene–light petroleum (1 : 19) yielded a white solid, which on crystallisation from methanol gave simiarenone as white crystals (0.004 5 g, 0.014%), m.p. 206—207° (lit.,[5] 207—208°), $[\alpha]_D^{27}$ +27.1° ($CHCl_3$) (lit.,[5] $[\alpha]_D$ +24°); $\nu_{max.}$ (KBr) 1 707 cm^{-1} (C=O), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c. comparison).

Isolation of Simiarenol.—Further elution with benzene–light petroleum (1 : 9) furnished a white solid, which on crystallisation from rectified spirit gave white crystals of simiarenol (0.030 g, 0.000 8%), m.p. 209—210° (lit.,[5] 210°), $[\alpha]_D^{27}$ +49.1° ($CHCl_3$) (lit.,[5] $[\alpha]_D$ +50°), R_F 0.35 (benzene); $\nu_{max.}$ (KBr) 3 440 cm^{-1} (OH), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c. comparison).

Isolation of Taraxerol.—Elution with benzene–light petroleum (1 : 4) gave a white solid which on crystallisation from light petroleum yielded taraxerol as white crystals (0.016 g, 0.004 5%), m.p. 283—284° (lit.,[6] 279—281°), $[\alpha]_D^{27}$ +4.2° ($CHCl_3$) (lit.,[6] $[\alpha]_D$ +3.1°), R_F 0.58 (chloroform); $\nu_{max.}$ (Nujol) 1 168 and 3 490 cm^{-1} (OH), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c. comparison).

Isolation of β-Sitosterol.—Elution of the column with benzene–light petroleum (1 : 1) gave white crystals of β-sitosterol (0.240 g, 0.074%), m.p. 136—137°, identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c. comparison).

Isolation of Betulinic acid.—Elution with chloroform benzene (1 : 1) furnished a gelatinous solid, which on crystallisation from methanol yielded white crystals of betulinic acid (0.33 g, 0.01%), m.p. 303—304° (lit.,[7] 309—310°), $[\alpha]_D^{27}$ +10.1° ($CHCl_3$) (lit.,[7] $[\alpha]_D$ +8°), R_F 0.70 [methanol–chloroform (1 : 19)]; $\nu_{max.}$ (KBr) 1 689 (CO_2H) and 3440 cm^{-1}(OH), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c. comparison).

Isolation of Myrtifolic Acid (1d).—The sodium hydroxide-soluble fraction (0.100 g) was chromatographed on a silica gel column (10 g). Elution with chloroform gave a solid which on crystallisation from light petroleum gave white shiny crystals of *myrtifolic acid* (1d) (0.028 g, 0.000 5%), m.p. 259—260°, $[\alpha]_D^{27}$ +13.7° (pyridine), R_F 0.43 [methanol–chloroform (1 : 19)] (Found: M^+, 456.360 3. $C_{30}H_{48}O_3$ requires M 456.357 7), positive response to Liebermann–Burchard test for a terpenoid; $\nu_{max.}$ (Nujol) 755, 829, 884, 930, 984, 1 002, 1 030, 1 067, 1 098, 1 140, 1 170, 1 230, 1 318, 1 377, 1 455, 1 678, 1 700, 2 900, and 3 350 cm^{-1}; *m/e* 456(8%), 441(15), 438(14), 423(40), 395(14), 301(7), 287(8), 273(7), 259(46), 255(16), 241(60), 235(54), 229(68), 221(30), 203(40), 189(62), 173(40), 159(48), 147(60), 135(70), 133(65), 121(98), 119(99), 109(98), 107(98), 95(95), 93(92), 91(74), 81(100), 69(99), and 55(99).

Methylation of Myrtifolic Acid.—Myrtifolic acid (0.020 g) in diethyl ether (10 ml) was treated with excess of diazomethane and left overnight. The residue obtained after evaporation on crystallisation from light petroleum, gave white crystals of *methyl myrtifolate* (1e) (0.020 g), m.p. 130—131°, $[\alpha]_D^{27}$ +8.2° ($CHCl_3$), R_F 0.27 (chloroform), M^+ 470, $\nu_{max.}$ 1 726 (CO_2Me) and 3 510 cm^{-1} (OH); τ ($CDCl_3$; 100 MHz) 4.62 (1 H, m, olefinic), 6.60 (3 H, s, ester CH_3), 6.72 (1 H, m, $W_{\frac{1}{2}}$ 2 Hz, C*H*·OAc), 8.10—8.80 (methylenes), 8.84 (3 H, allylic Me), 9.00, 9.02, 9.05, 9.13 (4 × 3 H, s, tert. methyls), and 9.13 (3 H, d, J 6 Hz) and 9.23 (3 H, d, J 5 Hz, two sec. methyls), *m/e* 470 (55%), 455(50), 435(15), 411(12), 395(6), 341(6), 331(7), 316(15), 315(13), 301(12), 273(12), 259(96), 255(20), 250(96), 247(98), 241(93), 235(36), 229(95), 220(46), 207(42), 203(55), 189(100), 187(48), 175(36), 173(34), 163(36), 161(38), 159(37), 147(95), 139(93), 133(92), 121(94), 119(95), 109(93), 107(93),105(94), 91(92), 81(92), and 69(94).

Oxidation of Myrtifolic Acid.—Myrtifolic acid (0.010 g) in pyridine (3 ml) was treated with chromic oxide (0.015 g) and left overnight. Work-up gave a solid which on crystallisation from light petroleum afforded white crystals of *myrtifonic acid* (1f) (0.009 g), m.p. 220—221°, $[\alpha]_D^{27}$ +5.1° ($CHCl_3$), M^+ 454, R_F 0.29 [methanol–chloroform (2 : 98)]; $\nu_{max.}$ ($CHCl_3$) 1 695 (CO_2H), 1 710 cm^{-1} (CO); o.r.d. (dioxan) $[\phi]_{260}$ +681pk, $[\phi]_{320}$ −1 530tr; *m/e* 454(2%), 439(14), 410(2), 409(2), 393(7), 371(16), 271(10), 257(90), 245(100), 235(90), 221(22), 218(20), 205(16), 203(15), 189(44), 121(60), 119(45), 109(34), and 95(90).

Reduction of Methyl Myrtifolate by Lithium Aluminium Hydride.—Methyl myrtifolate (0.010 g) in dry tetrahydrofuran (2 ml) was added slowly to a boiling solution of lithium aluminium hydride (0.050 g) in dry tetrahydrofuran (20 ml) and the mixture was maintined at 45 °C. After 3 h the reaction was stopped and the excess of hydride destroyed with ether. Work-up gave a solid which on crystallisation from light petroleum afforded white crystals of *myrtifolol* (1 g) (0.008 g), m.p. 275—276° (decomp.), $[\alpha]_D^{27}$ +20° ($CHCl_3$), R_F 0.24 [methanol–chloroform (2 : 98)] (Found: M^+, 442.3811. $C_{30}H_{50}O_2$ requires M, 442.3811); $\nu_{max.}$ (KBr) 1 350 and 3 300 cm^{-1} (OH); *m/e* 442(68%), 427(80), 411(92), 409(22), 393(6), 302(5), 301(5), 288(14), 287(12), 273(25), 271(25), 260(64), 259(90), 247(92), 241(93), 234(62), 230(90), 222(89), 221(90), 207(91), 203(87), 189(70), 179(54), 175(50), 173(51), 161(85), 147(87), 135(88), 133(89), 122(83), 105(88), 91(90), 79(92), and 69(87).

Oxidation of Myrtifolol.—Myrtifolol (0.005 5 g) in chloroform (1 ml) and acetic acid (2 ml) was added dropwise to a solution of chromic acid (0.030 g) in water (0.2 ml) and acetic acid (1 ml). After 1 h at room temperature methanol

was added, and the mixture was diluted with water and extracted with ether. The product was separated on a silica gel plate (5 g) with chloroform. The two u.v.-visible-absorbing bands were separated, extracted with chloroform, and crystallised from light petroleum. The more polar compound (0.001 6 g), m.p. 220—221° was identical with myrtifonic acid (1f) (mixed m.p. and t.l.c.). The less polar compound, *myrtifonal* (1h) (0.003 g), was a white crystalline solid, m.p. 160—161°, R_F 0.66 (chloroform), $\nu_{max.}$ (KBr) 1 074, 1 116, 1 190, 1 219, 1 300, 1 385, 1 450, 1 615, 1 670, 1 714, 1 722, 2 850, and 2 900 cm^{-1}.

Huang-Minlon Reduction of Myrtifonal.—Myrtifonal (0.002 8 g) and hydrazine hydrate (80%; 0.5 ml) in ethanol (5 ml) were heated under reflux for 3 h. Potassium hydroxide (0.300 g) in diethylene glycol (3 ml) was then added and the mixture was distilled until the internal temperature reached 205 °C. The mixture was then heated under reflux for 6 h, diluted with water, and extracted with ether. The crude product was separated on a plate of silica gel with light petroleum. The u.v.-visible absorbing band was extracted with light petroleum; evaporation left white crystals of bauerene (1a) (8 mg), m.p. 108—109°, R_F 0.95 (light petroleum), M^+ 410; $\nu_{max.}$ ($CHCl_3$) 1 372, 1 455, 1 468, 1 670, 2 850, and 2 900 cm^{-1}; *m/e* 410(48%), 395(15), 299(6), 286(7), 271(8), 257(25), 243(95), 232(95), 231(100), 205(55), 191(22), 177(20), 163(30), 149(40), 137(44), 123(90), and 109(91), identical with an authentic sample (mixed m.p., i.r. spectra, mass spectra, and t.l.c. comparison).

Methanol Extract of the Bark.—The methanol extract of the bark (295 g) was re-extracted with chloroform and then with ethyl acetate. Evaporation of the solvents gave a chloroform-soluble fraction (2.7 g, 0.049%) and an ethyl acetate soluble fraction (1.39 g, 0.023%). T.l.c. showed these two extracts to contain only traces of compounds isolated from the light petroleum extract.

Oxidation of Bauerenol.—Bauerenol (0.005 g) in pyridine (1 ml) was treated with chromic oxide (0.005 g) in pyridine (1 ml) and left overnight. Work-up and crystallisation from light petroleum gave white crystals of bauerenone (1b) (0.004 5 g), m.p. 238—239°, $[\alpha]_D^{27}$ −44.6° ($CHCl_3$) (lit.,[23] m.p. 240°, $[\alpha]_D$ −47.5°), R_F 0.50 (benzene); $\nu_{max.}$ (KBr) 1 708 cm^{-1} (CO).

Huang-Minlon Reduction of Bauerenone.—Bauerenone (0.004 g) and hydrazine hydrate (80%, 0.5 ml) were treated in the same way as above. Purification of the product on a silica gel plate gave bauerene as a white solid (0.002 8 g), m.p. 109—110°, R_F 0.95 (light petroleum); $\nu_{max.}$ ($CHCl_3$) 1 372, 1 453, 1 468, 1 670, 2 850, and 2 900 cm^{-1}; *m/e* 410(17%), 395(20), 299(2), 286(4), 271(5), 257(9), 243(20), 231(100), 205(15), 191(7), 183(7), 149(10), 137(15), 123(32), 109(36), 95(43), 83(32), 81(36), and 69(75).

Timber Extractives.—The hot light petroleum extract (2.1 g) in diethyl ether (200 ml) was washed with cold 5% sodium carbonate and 5% sodium hydroxide. The acidic and phenolic fractions on concentration yielded reddish brown solids (0.260 g, 0.004% and 0.157 g, 0.002 4%, respectively); the neutral fraction (1.6 g, 0.024%) was a pale reddish solid.

Isolation of Oleanolic Acid.—The phenolic fraction (0.157 g) was separated on a plate of silica gel $PG_{254-366}$ (25 g) with methanol–chloroform (1 : 19). The two bands visible under u.v. light were separated and extracted with chloroform. The less polar fraction on crystallisation from rectified spirit yielded white crystals of oleanolic acid (0.003 6 g, 0.000 06%), m.p. 307—308° (lit.,[19] 310°), $[\alpha]_D^{27}$ +78.5° ($CHCl_3$) (lit.,[22] $[\alpha]_D$ +80°) R_F 0.20 [methanol–chloroform (1 : 19)]; Liebermann–Burchard test gave a red colouration; $\nu_{max.}$ (KBr) 1 689 (CO_2H) and 3 400 cm^{-1} (OH), identical with an authentic sample (mixed m.p., i.r. spectra and t.l.c.). The more polar fraction on crystallisation from light petroleum gave more myrtifolic acid (0.038 g, 0.005 6%).

Isolation of β-Sitosterol.—The neutral fraction (1.5 g) was chromatographed on a column of silica gel (45 g). Elution with benzene gave β-sitosterol (0.130 g), m.p. 136—137° (from light petroleum) (lit.,[24] 136–137°).

Isolation of Jacareubin.—The methanol extract (200 g) was re-extracted with chloroform and then with ethyl acetate (Soxhlet). The chloroform extract gave 1.6 g (0.024%) and the ethyl acetate extract 1.3 g, (0.02%) of material. The chloroform extract by t.l.c. was shown to contain the same compounds as the hot light petroleum extract. The ethyl acetate extract (1.3 g) was separated on a column of silica gel (40 g). Elution with chloroform produced a yellow solid, which on crystallisation from light petroleum–chloroform (1 : 1) furnished yellow crystals of jacareubin (0.123 g, 0.001 9%), m.p. 253—254° (lit.,[20] 254—256°), R_F 0.19 [methanol–chloroform (3 : 97)]; $\lambda_{max.}$ (EtOH) 240 (log ε 4.10), 279 (4.60, and 334nm (4.26); $\nu_{max.}$ (KBr) 1 647 (CO) and 3 500 cm^{-1} (OH), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

We thank Professors R. H. Thomson (University of Aberdeen) and M. Shamma (Pennsylvania State University), Drs. J. K. Mcleod (Australian National University) and P. Bladon (University of Strathclyde), and Mr. M. J. Nagler (Tropical Products Institute, London) for the n.m.r. and mass spectral data; Professor F. N. Lahey (University of Queensland) for an authentic sample of bauerenol; Dr. J. S. Anderson and Mr. Paul Chai (Malaysian Forest Service) for a sample of *Mesua myrtifolia*; the University of Sri Lanka for a research assistantship (to S. P. G.); and Mrs. S. C. Weerasekera, Ms. S. Ramachandran, and Ms. D. V. Ariyapala for technical assistance. The research programme has been supported in part by a grant from the United States Department of Agriculture and in part by the National Science Council of Sri Lanka.

[6/1081 *Received*, 7th *June*, 1976]

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