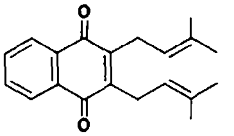
benzylic methylene groups (*d* at δ3·37, *J* 7 Hz), 2 vinyl protons (*t* at δ5·04, *J* 7 Hz) and four aromatic protons (2H, *m*, δ7·70–7·78; 2H, *m*, δ7·98–8·16). On the basis of these data the compound is considered to be 2,3-di(3,3-dimethylallyl)-1,4-naphthaquinone (1).



(1)

This structural assignment was confirmed by synthesis. Naphthalene-1,4-diol (30 g) was reacted with 2-methylbut-3-en-2-ol (30 g) in air, in refluxing 2% citric acid (1 L, 20 hr.). The reaction mixture was cooled, extracted with ether, washed with water, dried and concentrated. The concentrate was preparatively chromatographed (deactivated Si gel, benzene) and the first yellow band was collected, concentrated, and recrystallized as yellow needles (MeOH), mp 73–74° (9 g). This compound was identical in all respects with 1 (UV, IR, NMR, mmp).

Continued preparative chromatography (SiO_2, C_6H_6) of the *T. guayacan* pet. Et_2O solubles yielded small amounts of dehydro-α-lapachone, orange needles (MeOH) mp 148°; α-lapachone, yellow needles (MeOH) mp 116°; and β-lapachone, orange needles (MeOH) mp 155–156°. The identity of these compounds was determined by direct comparison to authentic samples and recorded values [3,4].

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TRITERPENOIDS AND FLAVONOIDS OF *DALBERGIA SERICEA* BARK

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Key Word Index—*Dalbergia sericea*; Leguminosae; triterpenoids; 3β, 16β-dihydroxy-olean-12en-29 or 30-oic acid; flavonoids; ψ-baptigenin; 7-hydroxy-6-methoxy-3',4'-methylenedioxyisoflavone; liquiritigenin; isoliquiritigenin.

Plant. Dalbergia sericea; *Geographical source*: Darjeeling (Himalayas). *Previous work.* Tirucallol acetate, glutinol, taraxerol and sitosterol from light petrol extract of the bark [1].

Present work. The air dried and ground bark (3·35 kg) was successively extracted with boiling light petrol (60–80°), C_6H_6, Me_2CO and alcohol. The light petrol and C_6H_6 extracts found to be similar (TLC), were mixed, concentrated and chromatographed over silica gel to yield 7 compounds, in the following order: (a) tirucallol acetate (1·3 g) from light petrol–C_6H_6, 9:1 eluates; (b) glutinol (350 mg) from light petrol–C_6H_6, 3:1 fraction; (c) taraxerol (650 mg) from light petrol–C_6H_6, 7:3 eluates; (d) sitosterol (500 mg) from benzene eluates; details of their identification have already been reported [1]. In addition C_6H_6–EtOAc, 10:1 fractions yielded a mixture, separated by rechromatography over silica gel to afford (e) erythrodiol (35 mg), mp 236–237°, $[\alpha]_D$ + 70·2° (*c*, 0·78, $CHCl_3$), positive LB, TNM tests, diacetate, mp 188–189° and (f) betulin (110 mg) as thin rectangular rods (MeOH), mp 254–255°, $[\alpha]_D$ +17·8° (*c*, 0·68, $CHCl_3$), positive LB, TNM tests, diacetate, mp 214–216°, $[\alpha]_D$ + 19·8 (*c*, 1·3 $CHCl_3$). Finally (g) a white waxy solid (85 mg) was eluted by C_6H_6–EtOAc, 5:2. ν_{max} (film) 1725 cm^{-1}, positive LB, TNM tests, gave sitosterol on saponification and was obviously an ester.

Acetone extract. On concentration and keeping in the refrigerator it deposited a solid (150 mg). This was purified on SiO_2 gel column to yield (h) ψ-baptigenin (120 mg) in C_6H_6–EtOAc, 3:2 eluates, mp 295–296°, gave negative tests for flavones and positive test for isoflavone; acetate, mp 163–164°, methyl ether, 177–178°; (i) another compound contaminated with (h) (15 mg) appeared in the later fractions of the same eluates. MS showed peaks in addition to those corresponding to (h), at 312 (M+), 298, 297, 229, 166, 156·5. These suggested (i) to contain an additional methoxyl as compared to (h) and the strong (M-15) peak suggested the location of the methoxyl at 6 [2,3] and hence (i) is considered to be 7-hydroxy-6-methoxy-3',4'-methylenedioxyisoflavone and this was confirmed by TLC with an authentic sample earlier reported from *D. riperia* [4] and *Pterodon apparicioi* [5].

The mother liquor from acetone extract on chromatography over silica gel afforded 5 more compounds: (j) from C_6H_6–EtOAc, 8:2 fractions, colourless needles (45 mg), mp 268–269° (MeOH), positive LB, TNM tests, ν_{max} (nujol) 3545, 1686, 1282, 1224, 1163, 1116, 1086, 1045, 1036, 1000, 890, 825, 808 & 726 cm^{-1}; MS (% abundance) M^+ 472(12), 454(10), 264(98), 246(99), 219(99), 218(78), 217(97), 207(100), 201(69), 175(81), 171(98), 149(69), 145(74), 131(97) and 121(96); (Found: C, 75·9;

H, 10·5. Calc. for $C_{30}H_{48}O_4$C, 76·2; H, 10·2%); diacetate with Py–Ac_2O at room temp, mp 183–185°, PMR ($CDCl_3$, δ) 0·87 (s, 9H), 1·00 (s, 6H), 1·17 (s, 3H), 1·27 (s, 3H), 2·1 (s, 6H), 5·35 (m, 1H); methyl ester diacetate, mp 170–171°, $[\alpha]_D$ +62·5 (c, 0·8 $CHCl_3$). These data indicated that (j) is a dihydroxy triterpene carboxylic acid with one hydroxyl and carboxyl in D/E rings (m/e 264) and one hydroxyl in A/B rings (m/e 207). The base peak in the mass spectrum at m/e 219 arises by a loss of C-28 function of Δ^2 oleananes. However, the facile alkaline hydrolysis (10% methanolic KOH, 5 hr) of methyl ester diacetate to give back the parent acid and absence of any methyl signal upfield from δ0·775 in PMR spectrum of acetate [6] ruled out its location on C-28, but the data were consistent with a C-29 or C-30 carboxyl function [7,8]. Of the two hydroxyls, both of which are secondary, one is likely to be at 3β-. In view of the easy acylation, the other hydroxyl could not be located at 15α-, β- or 16α-. Since MS data rule out its location in E ring, the only available position is 16β- and hence (j) could be 3β, 16β- dihydroxyolean-12-en-29- or 30-oic acid.

The remaining compounds identified were (k) isoliquiritigenin (25 mg), from C_6H_6–EtOAc (1 : 1) fraction followed by preparative TLC obtained as yellow prisms (EtOAc), mp 198–199°, deep brown colour with alc. $FeCl_3$, negative Shinoda and Wolfrom tests, λ_{max} (MeOH) 368 nm., confirmed by direct comparison (mmp, co-TLC and co-IR); (l) liquiritigenin (15 mg) as colourless rectangular plates (MeOH), mp 204–206°, negative ferric reaction and positive Shinoda's test, λ_{max} (MeOH) 230 (inf.), 276 nm, identical with cyclisation product of (k) with alc. HCl; (m) sitosterol-β-D-glucoside (120 mg) from C_6H_6–EtOAc (2 : 8) fractions as colourless rods (pyridine) mp 302–307° (d), positive LB, TNM, Molisch tests, acetate, mp 168–170°, $[\alpha]_D$ −30·7° (c, 0·825, $CHCl_3$) and finally (n) sucrose (250 mg).

The alcohol extract did not give any isolable material.

It would appear that the bark of *D. sericea* is specially rich in terpenoids as compared to other *Dalbergia* species.

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β-CITRAURINENE, A NEW C_{30}-CITRUS CAROTENOID*

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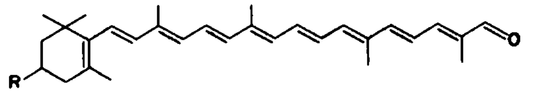
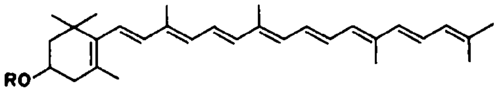
Key Word Index—*Citrus*; Rutaceae; carotenoid; β-citraurinene; 8′-apo-β-caroten-3-ol.

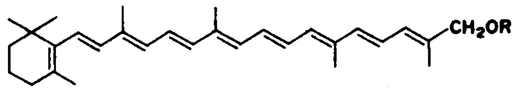
The pigment contributing mainly to the reddish and deep orange color in the peel of mandarins, oranges and many citrus hybrids is β-citraurin (3-hydroxy-8′-apo-β-caroten-8′-al) (**1**) [1,2]. The biosynthesis of β-citraurin in citrus peel was found to be greatly increased when harvested fruit was stored in an atmosphere containing up to 10 ppm ethylene and at temperatures below 30°. Simultaneously, 8′-apo-β-caroten-8′-al (**2**) increased to a lesser extent [2,3]. However, an unknown carotenoid was also found to greatly increase along with the two above mentioned C_{30}-pigments. Previously, it was thought to be cryptoxanthin, but later was found to be a mixture of cryptoxanthin and an unknown, with the unknown predominating in some cultivars. This unknown compound has been isolated from a citrus hybrid, Robinson (Orlando tangelo × Clementine), and identified by means of visible, IR, MS, NMR spectra and by chromatographic and chemical properties to be β-citraurinene (8′-apo-β-caroten-3-ol (**4**), a compound not believed to have previously been reported.



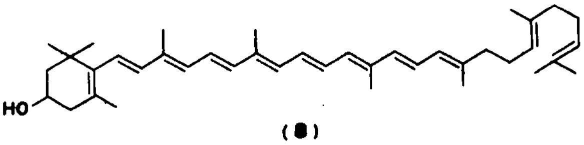
(**1**) R = OH (**2**) R = H



(**3**) R = acyl (**4**) R = H (**5**) R = Ac



(**6**) R = H (**7**) R = Ac



(**8**)

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