flame ionization detector Peak area percentages of each chromatogram were calculated by approximating the total area to 100%, by the use of an electronic integrator (Spectra Physics Auto Lab System) Retention indices were determined using *n*-alkanes (C_{26}–C_{36}) at an initial temp of 160° programmed at 2°/min The sterols were analysed as free alcohols and TMSi-derivatives TMSi ethers were prepared in the usual manner

Combined gas chromatography mass spectrometry The analyses were performed on a Varian 3 700 gas chromatograph–mass spectrometer (MAT 312) combination, equipped with a MAT 200 computer system

Authentic materials A sterol fraction consisting of campesterol, stigmasterol and sitosterol was supplied by the Riken Vitamin Oil Co, Tokyo, Japan Cholesterol was supplied by Fluka AG, Buch SG, and brassicasterol was supplied by Prof T Matsumoto (College of Science and Technology, Nihon University, Japan)

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QUAESITOL, A PHENOL FROM *GARCINIA QUAESITA*

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Key Word Index—*Garcinia quaesita*, Guttiferae, bark, hermonionic acid, quaesitol, α-spinasterol

Abstract—The petrol extractives of the bark of *Garcinia quaesita* gave hermonionic acid, its decarboxylated product and a new phenol, quaesitol

Bark extractives of *Garcinia quaesita* were chemically investigated by us [1] and we reported the isolation of hermonionic acid (**1**) and its decarboxylated product (**2**) We now report the characterisation of the most polar pigment, quaesitol (**3**), isolated from the hot petrol extractives of *G quaesita*

Quaesitol (**3**) had a molecular formula of $C_{33}H_{44}O_5$ (high resolution mass spectrum) The ^{1}H NMR spectrum showed the presence of the following signals (a) δ1 75, 1 65 and 1 55 (seven methyl groups of the type Me–C=), (b) 1 90 (two pairs of allylic protons), (c) 3 10–3 40 (six benzylic protons of the type $ArCH_2CH$=), (d) 3 70 (one methoxyl group), (e) 4 98–5 20 (four olefinic protons), (f) 5 90 (two aromatic protons) and (g) 6 30 (one aromatic proton) These data indicate the presence of two isoprenyl and one geranyl side chains as in **1** Acetylation of **3** with acetic anhydride–pyridine gave a triacetate showing the presence of three phenolic hydroxyl groups The mass fragmentation of **3** (Fig 1) showed significant fragments at *m/z* 465, 464, 397, 396, 327 and 175 The fragments at *m/z* 327 for **3** and for **1** isolated from the same source shows that both have identical ring A substitution The methoxyl group, the geranyl and isoprenyl chains of quaesitol should therefore be oriented in ring A The

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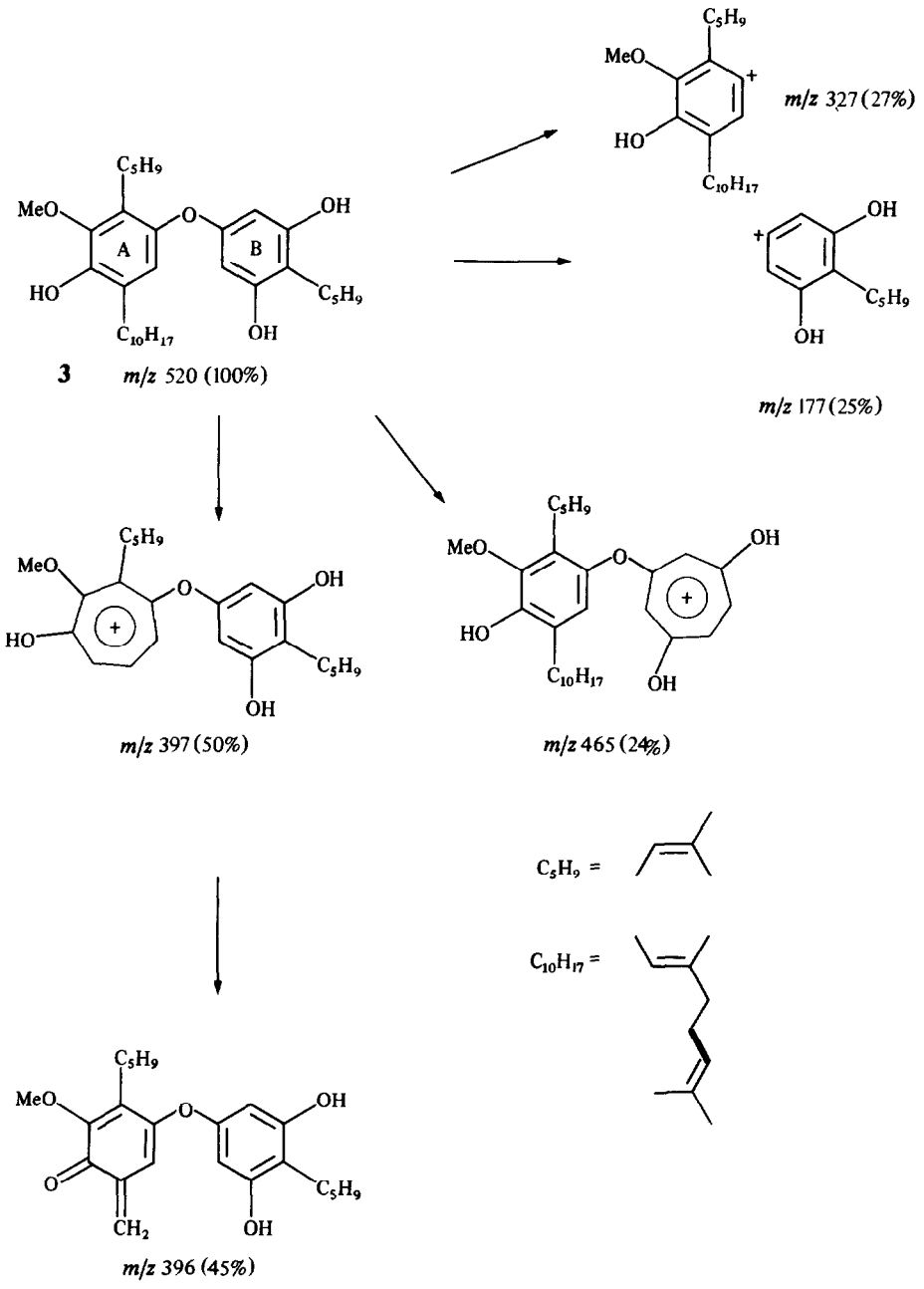
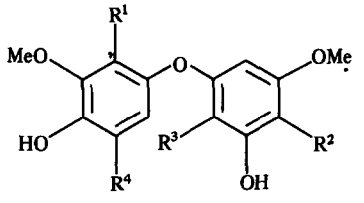
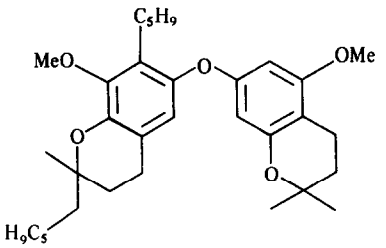


Fig 1 Mass fragmentations of quaesitol (3)



1 $R^1 = R^2 = C_5H_9$, $R^3 = CO_2H$, $R^4 = C_{10}H_{17}$
2 $R^1 = R^2 = C_5H_9$, $R^3 = H$, $R^4 = C_{10}H_{17}$

presence of the fragment ion at m/z 327 also requires the ring A to possess one of the hydroxyl groups with one aromatic proton unsubstituted Ring B should therefore contain the other two hydroxyl groups and the second isoprenyl group The two-proton singlet for aromatic protons at δ5 90 for **3** appeared at δ6 50 (2H, *s*) in the triacetate of **3** confirming the disposition of the two hydroxyl groups in ring B of **3** Quaesitol (**3**) is therefore identified as 1-*O*-[2-(3-methylbut-2-enyl)-3-methoxy-4-hydroxy-5-(3,7-dimethylocta-2,6-dienyl]-4-[3-methylbut-2-enyl]-3,5-dihydroxybenzene Thus quaesitol (**3**) is an *O*-demethyl derivative of **2** Hermonionic acid, **1**, which is a



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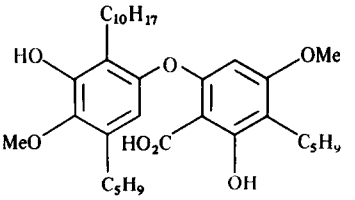

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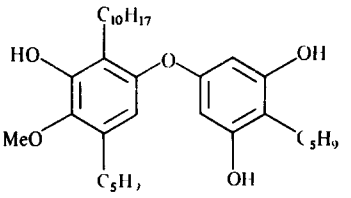

6

carboxy derivative of **2**, when treated with *p*-toluenesulphonic acid [1] gave a product which has been identified as **4** The formation of this product rules out the alternate structure **5** for hermonionic acid and also the alternate structure **6** for quaesitol In addition to **3**, α-spinasterol and 3β-acetoxy oleanolic acid were also isolated from the hot petrol extractives of the bark of *G quaesita*

EXPERIMENTAL

G quaesita was collected from the Kanneliya forest of Sri Lanka The dried, powdered bark (5 kg) gave 145 g of hot petrol extractives This when chromatographed over silica gel and elution with C_6H_6–petrol (1 1) [1] gave **2** followed by **1** Continued elution of the column with C_6H_6–petrol (3 2) yielded a gum which was purified by prep TLC to give **3** (0 01 %), $[\alpha]_D$ = 0 00, MW 520 3186 (MS), $C_{33}H_{44}O_5$ requires 520 3189, IR ν_{max} cm^{-1} 820, 850, 1020, 1040, 1150, 1250, 1430, 1470, 1600, 2900 and 3400; ^1H NMR (CCl_4, 60 MHz) δ6 30 (1H, *s*), 5 90 (2H, *s*), 4 98–5 20 (4H, *t*), 3 70 (3H, *s*), 3 10–3 40 (6H, *br*), 1 90 (4H, *s*), 1 75 (9H, *d*), 1 65 (9H, *s*), 1 55 (3H, *s*), MS *m/z* 520 ([M]$^+$, 100 %), 503 (26 6), 465 (24), 464 (20), 408 (13), 396 (45), 397 (50), 381 (90), 353 (33), 341 (53), 327 (27), 295 (33), 221 (48), 203 (27), 187 (36), 177 (25)

Acetylation of **3** Compound **3** (25 mg) was warmed at 100° with pyridine (5 ml) and Ac_2O (0 5 ml) for 30 min Usual work up gave the acetate of **3** ^1H NMR ($CDCl_3$, 60 MHz) δ6 60 (1H, *s*), 6 50 (2H, *s*), 4 9–5 1 (4H, *t*), 3 70 (3H, *s*), 3 30 (4H, *d*), 3 00 (2H, *d*), 2 20 (9H, *s*), 1 90 (4H, *s*), 1 70 (9H, *s*), 1 68 (9H, *s*) and 1 58 (3H, *s*)

Continued elution of the column gave 3β-acetoxy oleanolic acid, mp 257–258° (lit [2] 258–260°) identical with an authentic sample and α-spinasterol, mp 161–163° (lit [3] 164°), $[\alpha]_D$ −2 9° (lit [3] $[\alpha]_D$ −3 7°, identical with an authentic sample (mmp and co-TLC)

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