Chemical Investigation of Ceylonese Plants. Part III.[1] Extractives of the Fruits of *Argyreia Populifolia* Choisy (Convolvulaceae)

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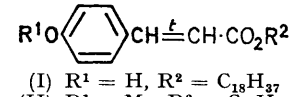
From the light petroleum extractives of the fruits of *Argyreia populifolia* Choisy, friedelin, friedelan-3β-ol, octacosan-1-ol, β-sitosterol, a new ester [stearyl 4-hydroxycinnamate (I)], and an unidentified ester have been isolated. Stearyl 4-methoxycinnamate (II) has been synthesised and shown to be identical with the methyl ether of the natural ester (I).

As part of studies on Ceylonese plants, the extractives of the fruits of the endemic plant *Argyreia populifolia* Choisy (Convolulaceae)[2] have been examined. Light petroleum extracts were separated into neutral and phenolic fractions. The neutral fraction was saponified and the nonsaponifiable fraction was separated on an alumina column. Five compounds were isolated: one was friedelin (m.p., mixed m.p., i.r., optical rotation, and t.l.c. comparison); another was friedelan-3β-ol (epifriedelanol) (m.p., mixed m.p., i.r., rotation, and t.l.c. comparison; acetate formation). The latter was oxidised with chromic acid to friedelin, identical with an authentic sample. A third compound was octacosan-1-ol (m.p., i.r., and mass spectrum), the fourth was β-sitosterol (m.p., i.r., rotation, and t.l.c. comparison; acetate formation), and the fifth (m.p. 72—73°) has not been identified.

The sodium hydroxide-soluble fraction gave a pale yellow phenolic solid (I), $C_{27}H_{44}O_3$, whose i.r. spectrum showed the presence of a hydroxy-group (3607 cm^{-1}), an αβ-unsaturated ester group (1717 cm^{-1}) and an aromatic system (1610 cm^{-1}). Absorption at 834 cm^{-1} indicated a 1,4-disubstituted benzene ring. The ready formation of a methyl ether (II) and an acetate (III) confirmed the presence of the hydroxy-group. On hydrogenation over palladised charcoal a dihydro-compound was obtained. Hydrolysis of compound (I) with alcoholic alkali gave 4-hydroxycinnamic acid (IV) (m.p., mixed m.p., and t.l.c. comparison with authentic sample) and stearyl alcohol (octadecan-1-ol;



(I) $R^1 = H$, $R^2 = C_{18}H_{37}$
(II) $R^1 = Me$, $R^2 = C_{18}H_{37}$
(III) $R^1 = Ac$, $R^2 = C_{18}H_{37}$
(IV) $R^2 = R^2 = H$

m.p., mixed m.p., i.r. and t.l.c. comparison with authentic sample) showing that compound (I) is stearyl 4-hydroxy-cinnamate. The u.v. data[3] of compound (I) and its

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derivatives and the n.m.r. spectrum of compound (I) supported the cinnamic ester structure.

Stearyl 4-methoxycinnamate was synthesised from 4-methoxycinnamoyl chloride and stearyl alcohol; the product was separated by chromatography on alumina and was identical with the methyl ether (II) of the natural product (m.p., mixed m.p., i.r., and mass spectra).

Higher fatty alcohol esters of 4-hydroxycinnamic acid have not apparently been isolated previously from plant sources, although wax alcohol esters of ferulic acid have been described.[4,5]

EXPERIMENTAL

M.p.s were taken on a Kofler hot-stage apparatus. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer, u.v. spectra on a Unicam SP 800 instrument, and n.m.r. spectra on a Perkin-Elmer R14 or a Varian 60 MHz spectrometer (deuteriochloroform solutions; tetramethylsilane as internal standard). Mass spectra were determined on an A.E.I. MS9 double-focusing spectrometer. Optical rotations were taken for solutions in chloroform (Billingham and Stanley polarimeter). Analytical and preparative t.l.c. was carried out with silica gel G (Merck) (thickness 0·25 and 1·00 mm, respectively). Column chromatography was carried out with silica gel (Koch-Light) and with alumina (Merck).

Extractives from the Fruits of Argyreia populifolia *Choisy.* —*Light petroleum extracts.* Finely ground dried fruits (1·8 kg) (collected from Peradeniya) were extracted with cold light petroleum (b.p. 40—60°; 10 l) for 10 days, and then with hot chloroform under reflux for 3 days. Evaporation of the light petroleum extracts afforded a dark brown oil (350 g, 19·5%), n_D^{25} 1·4705; acid number 27·4; saponification value 186·6; iodine number 68·6.

The oil (300 g) was dissolved in ether (500 ml) and washed with 10% sodium hydroxide (3 × 150 ml). The ether layer was washed with water, dried ($MgSO_4$), and evaporated to yield an oily liquid (A) (157·5 g, 10·2%). The sodium hydroxide washings were acidified with dilute sulphuric acid (10%) and extracted with ether. The ether layer was washed with 10% sodium carbonate solution (3 × 100 ml) to remove any fatty acids formed by cold saponification with sodium hydroxide. The ether layer was then washed with water, dried ($MgSO_4$), and evaporated to yield a pale yellow semi-solid (B) (15·0 g, 1·0%).

Chloroform extracts. Evaporation of the chloroform extracts yielded a brown semi-solid (90 g, 5·0%) which was refluxed with light petroleum (b.p. 60—80°) to remove light petroleum-soluble compounds (56·0 g, 3·1%). Analytical t.l.c. showed this fraction to be identical with the cold light petroleum extract. The light petroleum-insoluble fraction was a brown solid (19·0 g, 1·0%).

The Oil (A) from the Light Petroleum Extract.—The oil (A) (150 g) was saponified with ethanolic potassium hydroxide (0·5N; 500 ml) under reflux for 4 h to yield a non-saponifiable fraction (10 g, 0·7%). Analytical t.l.c. (benzene–chloroform, 1 : 1) indicated the presence of five compounds. This material was chromatographed on a column of alumina (300 g; activity I; neutral) made up in light petroleum (b.p. 60—80°). Elution was carried out with light petroleum containing increasing proportions of chloroform and finally with pure chloroform until no further material was eluted. Portions (50 ml) of the eluate were examined by analytical t.l.c. and combined as appropriate to yield five fractions.

Fraction 1. This fraction, eluted with light petroleum (b.p. 60—80°) and light petroleum–benzene (4 : 1), yielded a white solid (0·125 g, 0·009%). Crystallisation from light petroleum–benzene gave white needles of an unidentified ester, m.p. 72—73°, R_F 0·3 [light petroleum (b.p. 60—80°)] $\nu_{max.}$ (KCl) 3479 (bonded OH), 2934 and 2859, 1737 (saturated ester C=O), 1650 (C=C), 1460, 1169, 728, and 717 cm^{-1} τ($CDCl_3$; 60 MHz) 5·93 (2H, t, J 8 Hz, CO_2Me), 7·70 (2H, t, J 8 Hz, CH_2·CO), 8·73br (s, CH_2 protons), and 9·13br (6H, t, Me) (Found: C, 81·45, 81·6; H, 13·4; 13·55%).

Fraction 2. This fraction, eluted with light petroleum–benzene (1 : 1), yielded a white solid (0·200 g, 0·014%), which was crystallised from benzene–chloroform to give friedelin as needles, m.p. 250—254° (capill.), $[\alpha]_D^{25}$ −22·5° (*c* 0·33) (lit.,[6] m.p. 248—252°; $[\alpha]_D^{29}$ −27·5°); $\nu_{max.}$ (KBr) 2589·5, 2578, 1716 (C=O), 1460, and 1387 cm^{-1} [Found: C, 84·4; H, 11·9%; *M*(mass spec.), 426. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·85%; *M*, 426], identical (mixed m.p. and i.r. spectrum) with an authentic sample.

Fraction 3. This fraction, eluted with pure benzene, gave a white solid (0·35 g, 0·025%). Preparative t.l.c. gave friedelan-3β-ol as hexagonal crystals (from chloroform) (0·280 g, 0·02%), m.p. 274—276°, $[\alpha]_D^{25}$ +22·65° (*c* 0·33) (lit.,[7] m.p. 279—283°, $[\alpha]_D^{13}$ +24°); $\nu_{max.}$ (KCl) 3495 (OH), 2945, 2880, 1445, 1379, and 1170 cm^{-1} [Found: C, 83·0; H, 12·15%; *M*(mass spec.), 428. Calc. for $C_{30}H_{52}O$: C, 84·1; H, 12·15%; *M*, 428]. The acetate crystallised from benzene as white needles, m.p. 290—292° (capill.) $[\alpha]_D^{25}$ +45·0° (*c* 0·17) (lit.,[7] m.p. 290—294°, $[\alpha]_D^{13}$ +45°).

Friedelan-3β-ol (0·015 g) was oxidised with chromium trioxide (0·015 g) in pyridine (3·0 ml). The product (0·011 g, 73%) obtained after preparative t.l.c. was identical (m.p., mixed m.p., rotation, i.r. spectrum, and R_F) with friedelin.[7]

Fraction 4. This fraction, eluted with benzene–chloroform (1 : 2), afforded a white solid (0·050 g, 0·004%), which was crystallised from chloroform to yield octacosan-1-ol as white crystals, m.p. 80—82° (lit.,[8] 83—83·4°), R_F 0·4 (benzene–chloroform, 1 : 1); $\nu_{max.}$ (KBr) 3286 (OH), 2896, 1459, 1060, 730, and 720 cm^{-1} [Found: C, 81·55; H, 14·0%; *M*(mass spec.), 410. Calc. for $C_{28}H_{58}O$: C, 81·95; H, 14·15%; *M*, 410].

Fraction 5. This fraction, eluted with pure chloroform, gave needles (1·20 g, 0·085%) of β-sitosterol, m.p. 136—137°, $[\alpha]_D^{25}$ −37·0° (*c* 0·33) (lit.,[9a] m.p. 136—137°, $[\alpha]_D$ −36·6°). The acetate gave white needles (chloroform), m.p. 126—128°, $[\alpha]_D^{25}$ −45° (*c* 0·17) (lit.,[9a] m.p. 125—126°, $[\alpha]_D$ −41°).

The Semi-solid (B) from the Light Petroleum Extract.—The material (B) was chromatographed on acidic silica gel (200 g) prepared by washing silica gel with acetic acid

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(2%). Elution with chloroform afforded a pale yellow solid (1·0 g, 0·04%), which was purified by preparative t.l.c. to give faint yellow hexagonal crystals of *stearyl 4-hydroxycinnamate*, m.p. 99—100° (from chloroform), R_F 0·5 (chloroform–acetic acid, 60 : 1) $\lambda_{max.}$ (ethanol) 205 (ε 13,600), 230 (11,890), and 315 nm (12,370); $\nu_{max.}$ (CCl_4) 3607 (OH), 2930, 2860, 1716 (C=O of αβ-unsaturated ester), 1640 (C=C), 1610, and 1166 and 834 cm^{-1} (1,4-disubstituted benzene ring); τ ($CDCl_3$; 60 MHz) 2·54 (2H, d, *J* 18 Hz, aromatic 2- and 6-H), 3·14 (2H, d, *J* 8 Hz, aromatic 3- and 5-H), 2·34 (1H, d, *J* 16 Hz, ArC*H*=), 3·70 (1H, d, *J* 16 Hz, =CH·CO_2), 4·60br (1H, s, OH), 5·80 (2H, t, *J* 8 Hz, CO_2·CH_2), 8·20—8·73br (32H, m, CH_2 groups), and 9·00—9·15br (3H, t, Me) [Found: C, 77·6; H, 10·45%; *M*(mass spec.), 416. $C_{27}H_{44}O_3$ requires C, 77·8; H, 10·6%; *M*, 416]. The *acetate* gave white needles (from benzene–chloroform), m.p. 60—62°, R_F 0·8 ($CHCl_3$), $\lambda_{max.}$ (EtOH) 221 (ε 13,750) and 284 nm (21,120); $\nu_{max.}$ (CCl_4) 2930, 2860, 1746 (C=O of phenolic acetate), 1720 (C=O of αβ-unsaturated ester), 1644, 1200, and 1168 cm^{-1} [Found: *M* (mass spec.), 458. $C_{29}H_{46}O_4$ requires *M*, 458].

Stearyl 4-methoxycinnate. Stearyl 4-hydroxycinnamate (0·030 g) was dissolved in dry acetone (10 ml), and dimethyl sulphate (2 ml) and anhydrous potassium carbonate (2·0 g) were added. The mixture was refluxed overnight, cooled to room temperature, and filtered. Acetone was removed under reduced pressure to leave a brown oil, which was treated with ammonia (10%; 2 ml) in water (50 ml). A pale yellow solid was slowly deposited (0·028 g); this was filtered off and washed with water. Analytical t.l.c. (in benzene) of the product showed two spots, one of which was starting material. The other, R_F 0·6 (in benzene), was separated by preparative t.l.c. to give pure *stearyl 4-methoxycinnamate* as white needles (from chloroform) (0·020 g), m.p. 58—60°, $\lambda_{max.}$ (EtOH) (ε) 226·5 (ε 14,800) and 309 nm (25,680); $\nu_{max.}$ (CCl_4) 2930, 2860, 1714 (C=O of αβ-unsaturated ester), 1640 (C=C), 1610, 1250, and 1166·5 cm^{-1}; τ ($CDCl_3$; 60 MHz) 2·41 (2H, d, *J* 8 Hz, aromatic 2- and 6-H), 3·01 (2H, d, *J* 8 Hz, aromatic 3- and 5-H), 2·47 (1H, d, *J* 16 Hz, ArCH=), 3·66 (1H, d, *J* 16 Hz, =CH·CO_2), 5·80 (2H, t, *J* 8 Hz, CO_2CH_2), 6·15 (3H, s, OMe), 8·20—8·63br (32H, m, CH_2 groups), and 9·10br (3H, t, Me) [Found: *M*(mass spec.), 430. $C_{28}H_{46}O_3$ requires *M*, 430].

Hydrogenation of stearyl 4-hydroxycinnamate. The compound (0·030 g) was shaken in absolute ethanol (50 ml) with palladised charcoal (0·100 g) under hydrogen at atmospheric pressure for 4 h. Analytical t.l.c. showed the presence of essentially a single product. On removal of the catalyst and solvent the residual oil gradually crystallised to give white needles of *stearyl 3-(4-hydroxyphenyl)propionate* (0·022 g, 71%), m.p. 45—47°, R_F 0·7 (in chloroform), $\lambda_{max.}$ (EtOH) 223·5 (ε 6720) and 279 nm (1060); $\nu_{max.}$ (CCl_4) 3605 (OH), 2930, 2860, 1740 (C=O of saturated ester), 1615, 1175, and 1103 cm^{-1} [Found: C, 77·65; H, 10·65%; *M*(mass spec.), 418. $C_{27}H_{46}O_3$ requires C, 77·50; H, 11·00%; *M*, 418].

Hydrolysis of stearyl 4-hydroxycinnamate. The ester (0·100 g) was refluxed with ethanolic potassium hydroxide (10%; 200 ml) on a water-bath for 3 h. The cooled mixture was extracted with ether (300 ml). The ether layer was washed with water, dried ($MgSO_4$), and evaporated. The resulting white solid (0·038 g, 58%) crystallised from ethanol to give white flakes of stearyl alcohol, m.p. 59—60° (lit.,[10] 59—59·8°), $\nu_{max.}$ (CCl_4) 3615 (free OH), 2930, 2860, 1465, 1380, and 1050 cm^{-1}; τ ($CDCl_3$; 60 MHz) 6·35 (2H, t, *J* 6 Hz, CH_2·OH), 8·35—8·73br (32H, s, CH_2 groups), and 9·11 (3H, t, *J* 6 Hz, Me) [Found: C, 80·1; H, 14·0%; *M*(mass spec.), 270. Calc. for $C_{18}H_{38}O$: C, 80·00; H, 14·1%; *M*, 270], identical with an authentic sample (m.p., mixed m.p., i.r., R_F, and g.l.c.).

The alkaline solution obtained after hydrolysis and ether extraction was acidified with dilute hydrochloric acid (10%) and extracted with ether. The extract was washed with water, and dried ($MgSO_4$). Removal of ether left crystals of 4-hydroxycinnamic acid, m.p. 209—211° (lit.,[9b] 210—213°), identical with an authentic sample (m.p., mixed m.p., and R_F).

Synthesis of Stearyl 4-Methoxycinnamate.—4-Methoxycinnamic acid (2·5 g), prepared by the Knovenagel-Doebner reaction,[11] was treated with thionyl chloride (3·0 ml) and the mixture was heated on a water-bath for 1 h. Stearyl alcohol (2·0 g), obtained by the lithium aluminium reduction of stearic acid was then added to the resulting 4-methoxycinnamoyl chloride. The reaction was allowed to proceed for 2 h on a water-bath. Column chromatography on alumina (25·0 g; activity I; neutral) gave pure *stearyl 4-methoxycinnamate* as needles (0·5 g), m.p. 59—60° [Found: *M*(mass spec.), 430. $C_{28}H_{46}O$ requires *M*, 430], identical with the methylation product of stearyl 4-hydroxycinnamate (mixed m.p., R_F, i.r., and mass spectra).

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