(2144), 339(2465). IR_{KBr} cm^{-1} 3230, 3060, 2820—2000, 1715, 1680, 1605, 1440, 1355, 1190, 1165. NMR in *d*-DMSO δ ppm 3.89 (3H, singlet), 6.69 (1H, doublet, $J=3.0$), 6.94 (1H, doublet, $J=3.0$), 7.58 (1H, singlet), 10.89 (1H, singlet). Mass Spectrum *m/e*: 236 (M^+, 88%), 191 (100%), 135 (47%).

Methylation of Ia——Suspended 15 mg of Ia in 50 ml of methanol and added ether solution of diazomethane upon it. After 1 day, solvent was evaporated and 16 mg of Ib was obtained. Recrystalized from methanol.

Ib——Colorless needles, mp 203—204° from methanol. Insoluble in most organic solvents. Slightly soluble in methanol and ethanol. UV λ_{max}^{EtOH} nm (ε) 254.5(35494), 309.5(3509), 327(2948), 339(2679). IR_{KBr} cm^{-1} 3090, 2940, 1733, 1708, 1595, 1464, 1370, 1283, 1199. NMR in *d*-DMSO δ ppm 3.88(3H, singlet), 3.92 (6H, singlet), 6.80(1H, doublet, $J=2.5$), 7.01(1H, singlet). Mass Spectrum *m/e*: 264.0625 (Calcd.: 264.2370 (M^+, 78%), 205(100%), 149(50%).

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On the Constituents of Seeds of *Horsfieldia iryaghedhi* Warb. I

Isao Kitagawa, Tsutomu Nakanishi, Yoshihisa Ito,[1a] M.U.S. Sultanbawa,[1b] and Itiro Yosioka[1a]

Faculty of Pharmaceutical Sciences, Osaka University[1a] *and Department of Chemistry, University of Ceylon*[1b]

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The seeds of *Horsfieldia iryaghedhi* Warb. (=*Myristica horsfieldia*, *M. iryaghedhi*) (Myristicaceae), an indigenous plant to Ceylon, are about 1.5 inches of oblong shape and are little smaller in size than the seeds of *Myristica fragrans* Houttuyn (nutmegs). Although the chemical constituents of nutmegs have been investigated extensively due to its pharmaceutic necessity (*e.g.* as an ingredient in Aromatic Rhubarb Tincture or a condiment),[2] no work has been provided on the seeds of *H. iryaghedhi*. The present paper is concerned with the isolation of *d*-asarinin (I) and dodecanoylphloroglucinol (IIa) from the seeds.[3]

The fractionation was undertaken as shown in Chart 1. The unsaponifiable portion obtained from the neutral fraction afforded a substance, mp 122.5—123°, whose physical data (ultraviolet (UV), infrared (IR), proton magnetic resonance (PMR), and mass spectra, and $[\alpha]_D$) are in good accord with those of *d*-asarinin (I),[4] and it was identified with the authentic sample[5] by the direct comparison. Minute examination of the cold methanol extract of the seeds by thin-layer chromatography (TLC) disclosed that the seeds do not contain *d*-sesamin[5,6] which has been known to isomerize to *d*-asarinin on acid treatment at reflux.[4b] The saponified portion was disclosed to consist of myristic and lauric acids by mass spectrometry and gas-liquid chromatography (GLC, as methyl esters). The alkali soluble fraction

1) Location: *a*) *Toneyama, Toyonaka, Osaka*; *b*) *Peradeniya, Ceylon.*
2) E.P. Claus and V.E. Tyler, Jr., "Pharmacognosy," 5th ed., Lea & Febiger, Philadelphia, 1965, p. 223.
3) Presented at the 21st Annual Meeting of Kinki Branch, Pharmaceutical Society of Japan, Osaka November 1971, Abstract Papers, p. 22.
4) *a*) E.D. Becker and M. Beroza, *Tetrahedron Letters*, **1962**, 157; *b*) K. Takahashi and T. Nakagawa, *Chem. Pharm. Bull.* (Tokyo), **14**, 641 (1966); *c*) A. Pelter, *J. Chem. Soc.* (*C*), **1967**, 1376; *d*) A.M. Duffield, *J. Heterocyclic Chem.*, **4**, 16 (1967); *e*) L.V. Tutupalli and M.G. Chaubal, *Phytochemistry*, **10**, 3331 (1971).
5) Kindly provided by Prof. K. Takahashi of Kanazawa University.
6) W.A. Jones, M. Beroza, and E.D. Becker, *J. Org. Chem.*, **27**, 3232 (1963).

comprises several components as detected by TLC. However, it has been revealed that the major and slow moving components are quite unstable and change remarkably (probably due to light and/or air-oxidation) to the discolored substances while silica gel column chromatography. We have not yet succeeded in the isolation of major components, but obtained a minor constituent (less polar and termed as ML-1) of mp 125—126° whose structure has been assigned as dodecanoylphloroglucinol (IIa)[7] on the basis of the following evidence. ML-1 also discolors gradually on standing for a long while.

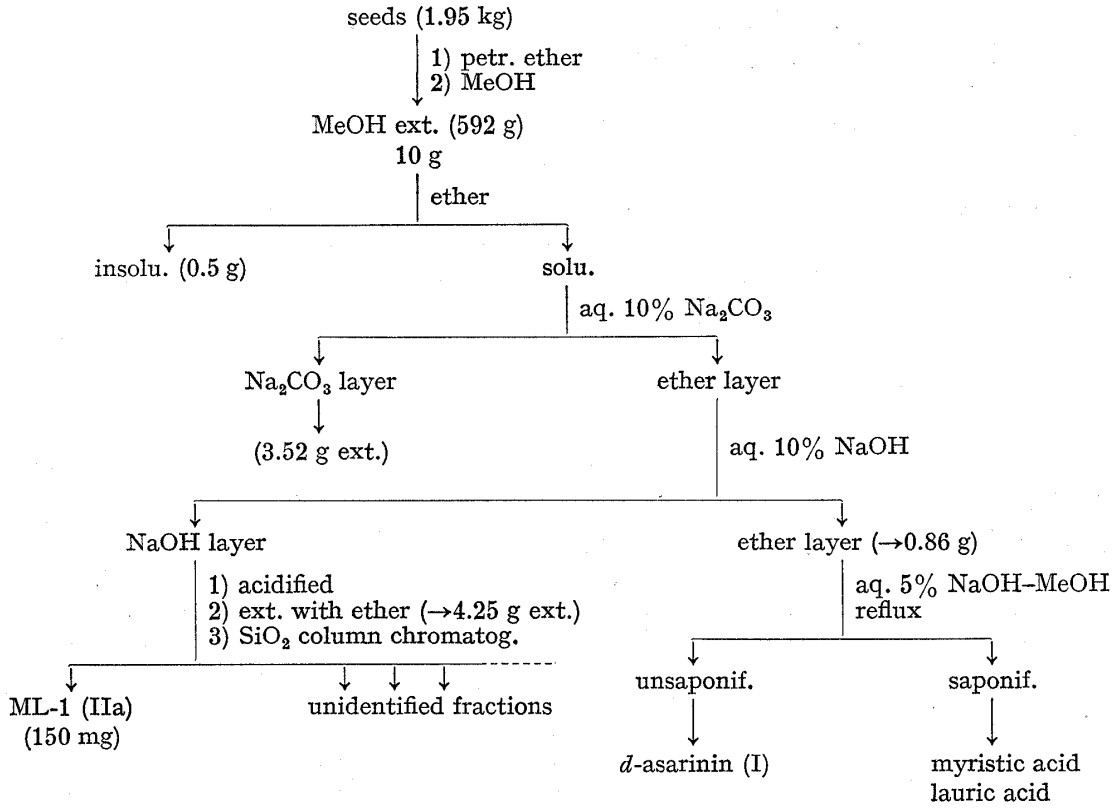
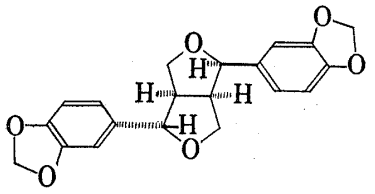
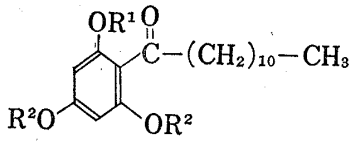


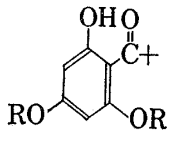
Chart 1



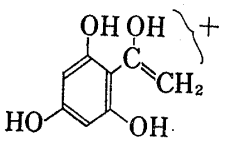
I : *d*-asarinin



IIa : $R^1=R^2=H$ (=ML−1)
IIb : $R^1=H, R^2=CH_3$
IIc : $R^1=R^2=Ac$



a : R=H (*m/e* 153)
b : $R=CH_3$ (*m/e* 181)



c : *m/e* 168

Chart 2

7) I. Inagaki, S. Hisada, M. Ogawa, and Y. Noro, *Yakugaku Zasshi*, **76**, 1253 (1956).

ML-1, $C_{18}H_{28}O_4$ (M^+: *m/e* 308), has been considered to be a phenolic derivative having a dodecanoyl side chain as based on its IR (3380, 3250 (hydroxyl), 1640 (sh., chelated carbonyl), and 1609 cm^{-1} (phenyl)) and PMR (4.07 τ (2H, s, phenyl ring protons), 9.12 (3H, t-like, terminal methyl), 8.70 (18H, br.s, methylene side chain) and 6.92 (2H, t, J=7 Hz, active methylene)) spectra along with its positive property for $FeCl_3$. ML-1 gave a dimethylether (IIb) and a triacetate (IIc). The physical properties of IIb and IIc show that ML-1 possesses three phenolic hydroxyls (three phenolic acetoxyl functions at 1783 cm^{-1} and at 7.84 (6H) and 7.78 τ (3H) in IIc) of which at least one is located at *ortho* position to the dodecanoyl function (1640 cm^{-1} in ML-1 and 1704 cm^{-1} in IIc). The UV spectrum of ML-1 discloses that ML-1 carries a 2,4,6-trihydroxyphenylketone chromophore.[8] The accumulated data have led to an assumption that ML-1 is dodecanoylphloroglucinol (IIa). The *meta* coupling protons of IIb at 4.05 and 4.21 τ (2H, AB quartet, J=2 Hz), mass spectra of ML-1 and IIc both giving the same base peak at *m/e* 153 (ion a) and that of IIb giving a base peak at *m/e* 181 (ion b) support the assumption. Finally, the correctness of assignment was proved by the direct comparison with the authentic sample.[9] This seems to be the first occurrence of dodecanoylphloroglucinol (IIa) in nature. The chemical constitution of other components will be the subject of further investigation.

Experimental[10]

Isolation of *d*-Asarinin, Myristic Acid, and Lauric Acid——The neutral fraction (0.86 g) obtained as shown in Chart 1 was crystallized twice from MeOH. Since the product (190 mg) was revealed to be a mixture by TLC (detected by I_2 vapor), it was treated with 5% NaOH–MeOH (10 ml) at reflux for 4 hr, poured into water, and extracted with ether. Evaporation of the solvent followed by crystallization from MeOH furnished colorless needles (73 mg) of mp 122.5—123°. $[\alpha]_D$ +138° (c, 0.9 in $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.72; H, 4.96. UV λ_{max}^{EtOH} nm (ε): 237 (10028), 287 (9143). IR ν_{max}^{KBr} cm^{-1}: 1610 (phenyl). PMR ($CDCl_3$) τ: 6.91—6.55 (2H, m), 6.40—5.85 (4H, m), 5.65 (1H, d, J=7.5 Hz), 5.24 (1H, d, J=5.0 Hz), 4.13 (4H, s), 3.20—3.13 (6H, m). Mass Spectrum (*m/e*, %): 354 (M^+, 100), 203 (56), 179 (51), 161 (59), 150 (59), 149 (76). The compound was identified with authentic *d*-asarinin (I)[5] by mixed mp, TLC, IR, and mass spectra.

The aqueous layer after extraction with ether was acidified with HCl and extracted with ether. The ether soluble portion (32 mg) was then purified by preparative TLC (SiO_2, Camag D-5) to give crystals of mp 36°. IR ν_{max}^{Nujol} cm^{-1}: 1710 (COOH). Mass Spectrum (*m/e*, %): 228 (M^+ of myristic acid, 100), 200 (M^+ of lauric acid, 81), 199 (44), 185 (86), 171 (73), 157 (75), 143 (69). After methylation with diazomethane, the product was identified with a mixture of methyl myristate and methyl laurate by GLC (1.5% SE-30 at 150° and 3% PEGS at 140°).

Isolation of Dodecanoylphloroglucinol (=ML-1) (IIa) and Preparation of Its Derivatives——The NaOH layer obtained as given in Chart 1 was neutralized with aq. 10% HCl and extracted with ether. The residue (4.25 g) obtained by evaporation of the solvent was chromatographed on silica gel (Merck, 150 g) eluting with benzene–AcOEt mixtures. The compound obtained from earlier elution of benzene–AcOEt (20:1) mixture was crystallized from $CHCl_3$ quickly to give ML-1 (150 mg) of mp 125—126° (colorless plates). Prolonged heating should be avoided on crystallization, otherwise discoloration occurs (bath temp. below 70°). Mass (*m/e*, %): 308 (M^+ of $C_{18}H_{28}O_4$, 5.4), 181 (21), 168 (c, 36), 153 (a, 100). UV λ_{max}^{EtOH} nm (ε): 228 (14500), 288 (18800). PMR (d_6-acetone) τ: −1.55—0.12 (2H, br., O<u>H</u>×2, exchangeable with D_2O) and other signals as given in the text. ML-1 was identified with dodecanoylphloroglucinol (IIa)[9] by mixed mp, UV, IR (Nujol) and TLC. Methylation of IIa with diazomethane in EtOH at room temperature followed by crystallization from MeOH furnished a dimethylether (IIb), mp 79—82°. Mass Spectrum (*m/e*, %): 336 (M^+ of $C_{20}H_{32}O_4$, 7), 196 (20), 181 (b, 100). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3100—2500 (chelated OH), 1620, 1600 (sh.) (chelated CO and phenyl ring). PMR (CCl_4) τ: 9.10 (3H, t-like, -CH_2-C<u>H</u>$_3$), 8.72 (18H, br. s, -(C<u>H</u>$_2$)$_9$-), 7.10 (2H, t, J=7

8) A.I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, Oxford, London, 1964, p. 105.
9) Kindly provided by Prof. I. Inagaki of Nagoya City University.
10) The following instruments were used for the physical data. Melting points: Yanagimoto Micro-melting point Apparatus (a hot-stage type); UV spectra: Shimadzu MPS-50L UV Spectrometer; IR spectra: Hitachi IR Spectrometers EPI-G3 and EPI-S2; PMR spectra: Varian A-60 NMR Spectrometer; Mass spectra: Hitachi RMU-6D Mass Spectrometer; GLC: Yanagimoto Gas Chromatograph GCG-3DH.

Hz, -CO-C$\underline{H}_2$-CH_2-), 6.22, 6.16 (3H. each, s, -OC$\underline{H}_3$×2), 4.21, 4.05 (2H, ABq, J=2 Hz, phenyl ring protons at *meta* disposition).

Acetylation of IIa with Ac_2O and pyridine at room temperature for 48 hr afforded a triacetate (IIc, amorphous). Mass Spectrum (*m/e*, %): 434 (M^+ of $C_{24}H_{34}O_7$, 0.1), 392 (4), 350 (17), 308 (4), 168 (c, 51), 153 (a, 100). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1783, 1182, (acetate) 1704 (CO), 1616 (phenyl). PMR (CCl_4) τ: 9.10 (3H, t-like, -CH_2-C$\underline{H}_3$), 8.72 (18H, br. s, -$(CH_2)_9$-), 7.84 (6H, s, OAc×2), 7.78 (3H, s, OAc), 7.37 (2H, t, J=7 Hz, -CO-C$\underline{H}_2$-CH_2-), 3.15 (2H, s, phenyl ring protons).

Successive elution with benzene–AcOEt (20:1) mixtures afforded the unstable major components whose purification has not yet been accomplished.

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