Isolation of the constituents of Kielmeyera candidissima. Powdered trunk wood (6·1 kg) was extracted with benzene. The solvent was evaporated and the residue (18 g) was chromatographed on silica. Upon elution with solvent of gradually increasing polarity, appeared in order an aliphatic ester (100 mg), sitosterol (2 g), 1,7-dihydroxyxanthone (100 mg),[6] 1,3-dihydroxy-2,8-dimethoxyxanthone (15 mg) and 1,3-di-methoxy-5-hydroxyxanthone (20 mg).[7]

1,3-Dihydroxy-2,8-dimethoxyxanthone, was obtained from EtOH as yellow crystals, m.p. 313–317° (sealed capillary), 320° dec. (Kofler block). λ_{max}^{EtOH} (nm): 224, 252, 296, 315, 371 (ε 13 100, 16 100, 5600, 5700, 6500); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 230, 245sh, 380 (ε 22 450, 16 250, 15 250); $\lambda_{max}^{EtOH+NaOH}$ (nm): 225, 260sh, 283, 345 390 (ε 20 400, 8400, 5300, 6200, 11 100); $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 223, 252, 280, 321 (ε 15 100, 12 100, 9150, 8350. Gibbs test[5] λ_{max} (nm): 430, 685 (Absorbance 0·14, 0·35). ν_{max}^{KBr} (cm^{-1}): 3270 (broad) 1649, 1603, 1578, 1291, 1156. MS: M, Found: 288·0630. Calc. for $C_{15}H_{12}O_6$: 288·0634. M 288 (5%), *m/e* (%) 273 (1) [M-15, m* obs. 258, calc. 258·8], 258 (100) [M-30, m* obs. 231, calc. 231·1], 243 (35) [(M-15)−30, m* obs. 243, calc. 243·7], 229 (6), 215 (9), 187 (9), 129 (8), 115 (2).

1-Hydroxy-2,3,8-trimethoxyxanthone. Methylation of above compd. with CH_2N_2 gave yellow crystals, m.p. 171–173° (EtOH). λ_{max}^{EtOH} (nm): 252, 292, 370 (ε 47 700, 17 050, 14 950). No alteration in presence of NaOAc. $\lambda_{max}^{EtOH+NaOH}$ (nm): 236, 276 (ε 42 900, 35 350). $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 255, 282, 313 (ε 35 350, 25 350 18 850).

1,2,3,8-Tetramethoxyxanthone. Methylation in acetone with Me_2SO_4 and K_2CO_3 (reflux, 24 hr), gave a mixture of tri- and tetramethyl ether which was separated by chromatography on silica. Tetramethyl ether was obtained as colourless crystals, m.p. 199–201° (EtOH). λ_{max}^{EtOH} (nm): 249, 285, 361 (ε 33 150, 11 500, 11 050). No alteration in presence of NaOH or $AlCl_3$.

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[6] O. R. GOTTLIEB and G. M. STEFANI, *Phytochem.* **9**, 453 (1970).
[7] O. R. GOTTLIEB, M. TAVEIRA MAGALHÃES, M. CAMEY, A. A. LINS MESQUITA and D. DE BARROS CORRÊA, *Tetrahedron* **22**, 1777 (1966).

Key Word Index—Kielmeyera candidissima; Guttiferae; sitosterol; euxanthone; 1,3-dimethoxy-5-hydroxyxanthone; 1,3-dihydroxy-2,8-dimethoxyxanthone.

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TRITERPENOID CONSTITUENTS OF *CLUSIA ROSEA*

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Plant. Clusia rosea. Source. Caripe, situated at an altitude of 600 m south-east of Cumana. *Uses.* The resinous material of the plant was used for curing bone fractures.[1] *Previous work. Kielmeyera rosea* has been reported[2] to contain friedelin, sitosterol, β-amyrin and *n*-triacontanol.

Present work. The powdered plant material was extracted with light petroleum and the extract was chromatographed on alumina (activity III) and following fractions collected; (1) light petroleum (A_1), (2) benzene (A_2), (3) $CHCl_3$ (A_3), and (4) MeOH (A_4). From these fractions the following compounds were isolated:

[1] H. PITTIER, *Manual de las plantas usales de Venezuela y su suplemento*, p. 211, Fundacion Eugenio Menzoza, Caracus (1970).
[2] F. S. SILVA, *An. Acad. Brasil Cienc.* **40** (2), 155 (1968).

Aplotaxene. To a light petroleum solution of the fraction (A_1) was added MeOH dropwise, a white precipitate was formed; the filtrate on concentration gave aplotaxene b.p. 110–115° (bath)/8 mm; n_D^{27}, 1·4835. IR bands at: 2950, 1650, 1460, 1455, 1380, 1215, 1144, 1122, 1048, 999, 905, 890, 836, 815, 781 cm^{-1}. (Found: C, 88·10; H, 12·03. Calc. for $C_{17}H_{28}$: C, 87·93; H, 12·07%.)*

Friedelin. The fraction (A_2) was chromatographed on alumina and following fractions were collected; (1) light petroleum (B_1), and (2) benzene (B_2). The fraction (B_1) after concentration was left at 0° overnight, crystals separated. It was recrystallized repeatedly with benzene and was found to be friedelin. M.p. 239–241°, $[\alpha]_D$, −22° (c, 1·5, $CHCl_3$). IR band at 1710 cm^{-1}. The NMR, MS[3] and the ORD curve[4] were identical with those of the friedelin. (Found: C, 84·54; H, 11·64. Calc. for $C_{30}H_{50}O$: C, 84·43; H, 11·81%.)

α- and β-Friedelinols. The $CHCl_3$ fraction (A_3) was diluted with light petroleum and on cooling at 0° for 72 hr gave a crystalline compound. TLC of the compound over $AgNO_3$ impregnated silica gel[5] using benzene–$CHCl_3$ (1:1) showed two spots very close to each other. The IR spectrum indicated a prominent band at 3500 cm^{-1} due to —OH. This mixture was oxidized with Jones reagent[6] to give a ketone (IR band at 1710 cm^{-1}) which showed following properties: m.p. 237–238°, $[\alpha]_D$, −36·0° (c, 0·56, $CHCl_3$). The m.m.p. with an authentic sample[7] of friedelin was undepressed. The formation of only friedelin by the oxidation of the mixture of alcohols indicates that the mixture contains α-friedelinol and β-friedelinol.

Oleanolic acid. After removal of the friedelinole from the fraction (A_3), the residue was further cooled at 0° for 2 weeks. The acid was deposited as yellow amorphous powder. The crude acid was subjected to repeated sublimations till pure material was obtained. It showed following properties: m.p. 310–311°; $[\alpha]_D$, +80·5° (c, 0·54, $CHCl_3$). IR bands: 3400, 2930, 1700, 1650, 1460, 1240, 1180, 1108, 980, 880 cm^{-1}. (Found: C, 78·64; H, 10·50. Calc. for $C_{30}H_{48}O$: C, 78·94; H, 10·52%.) (Literature reports[8] m.p. 306–307°, $[\alpha]_D$, +77°.)

Sitosterol. This was also isolated from the fraction (A_3) and showed following properties: m.p. 134·5–135°; $[\alpha]_D$, −35·8° (c, 1·5, $CHCl_3$) IR bands: 1760, 1655, 1437, 1376, 1280, 1242, 1152, 951, 890, 815 cm^{-1}. (Found: C, 84·21; H, 12·32. Calc. for $C_{29}H_{50}O$: C, 83·99; H, 12·15%.)

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[3] The NMR and the mass spectra were kindly taken by Professor G. OURRISON, at Institut de Chimie, Strasbourg.

[4] The ORD curve was kindly taken by Professor W. KLYNE of Westfield College, London.

[5] A. S. GUPTA and S. DEV, *J. Chromatog.* **12**, 189 (1963).

[6] K. BODWEN, I. M. HEILBORN, E. R. H. JONES and B. C. L. WEEDON, *J. Chem. Soc.* **39** (1946); A. BOWERS, T. G. HALLSALL, E. R. H. JONES and A. J. LEMIN, *ibid.* 2555 (1943).

[7] The author is grateful to the Department of chemistry, University of Tokyo, Tokyo for providing authentic sample of friedelin.

[8] *Elsevier's Encyclopaedia of Organic Chemistry* (edited by E. JOSEPHY and F. RADT), Vol. 14, p. 539, Elsevier, New York (1940).

Key Word Index—*Clusia rosea*; Guttiferae; aplotaxene; friedelin; α- and β-friedelinol; oleanolic acid; sitosterol.