

GUTTIFERAE

XANTHONES FROM A *KIELMEYERA* SPECIES*

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On wooded land near the seashore between Linhares and São Mateus, Espírito Santo, Brasil, A. P. Duarte located a seemingly new arboreous *Kielmeyera* species. Material was deposited under the provisional designation *K. candidissima* A. P. Duarte at the Herbarium of the Museum of Natural History, Federal University of Minas Gerais, Belo Horizonte, specimen No. 000616.

Examination of the trunk wood of *K. candidissima* revealed the presence of sitosterol, 1,7-dihydroxyxanthone (euxanthone), 1,3-dimethoxy-5-hydroxyxanthone and of a new yellow compound whose molecular formula, $C_{13}H_4O_2(OH)_2(OMe)_2$, was compatible with a xanthone structure. It was easily transformed into a yellow monomethyl ether by treatment with CH_2N_2 . The considerable acidity of the compound was also apparent from the UV spectrum; addition of NaOAc produced the strong batho- and hyperchromic shifts which are typical of 3-hydroxyxanthones, bearing an additional oxy-function at one of the vicinal 2 or 4-positions.² By contrast, vigorous conditions had to be employed to achieve even partial transformation into a dimethyl ether. This fact is diagnostic of a sterically hindered *peri*-hydroxyl.³ In the present case, the bulky substituent can only be a vicinal methoxyl. The NMR spectrum of the di-*O*-methyl derivative defined conclusively⁴ the location of three vicinal hydrogens at C-5,6,7 (τ 2.96, 2.43 and 3.20, three quartets), and indicated the presence of the fourth aromatic hydrogen either at C-2 or at C-4 (τ 3.13, singlet). At this stage the vicinality of both, the 3-hydroxyl and the *peri*-hydroxyl, with a methoxyl had already been established; a lone methoxyl having to be placed at the alternative *peri*-position, the constitution 1,3-dihydroxy-2,8-dimethoxyxanthone emerged for the new compound.

The proposal was consistent with two further data: A feebly positive Gibbs test, characteristic of 1,3-dihydroxyxanthones;⁵ and the UV spectrum which is closely comparable to the spectrum of 1,6-dihydroxy-7,8-methylenedioxyxanthone,¹ the only known natural xanthone with the same oxygenation pattern.

EXPERIMENTAL

For experimental techniques see ref. 2. All known compds. were identified by direct comparison with authentic samples.

* Part XXIX in the series "The Chemistry of Brazilian Guttiferaes". For part XXVIII see ref. 1

¹ R. ALVES DE LIMA, O. R. GOTTLIEB and A. A. LINS MESQUITA, to be published.

² D. DE BARROS CORRÊA, L. G. FONSECA E SILVA, O. R. GOTTLIEB and S. JANOT GONÇALVES, *Phytochem.* **9**, 447 (1970).

³ M. L. WOLFROM, F. KOMITSKY, JR. and P. M. MUNDELL, *J. Org. Chem.* **30**, 1088 (1965).

⁴ D. BARRACLOUGH, O. R. GOTTLIEB, H. D. LOCKSLEY, F. SCHEINMANN and M. TAVEIRA MAGALHÃES, *J. Chem. Soc. B*, 603 (1970).

⁵ A. A. LINS MESQUITA, D. DE BARROS CORRÊA, O. R. GOTTLIEB and M. TAVEIRA MAGALHÃES, *Anal. Chim. Acta* **42**, 311 (1968).

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-dimethoxy-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). $\lambda_{\text{max}}^{\text{EtOH}}$ (nm): 224, 252, 296, 315, 371 (ϵ 13 100, 16 100, 5600, 5700, 6500); $\lambda_{\text{max}}^{\text{EtOH}+\text{NaOAc}}$ (nm): 230, 245sh, 380 (ϵ 22 450, 16 250, 15 250); $\lambda_{\text{max}}^{\text{EtOH}+\text{NaOH}}$ (nm): 225, 260sh, 283, 345 390 (ϵ 20 400, 8400, 5300, 6200, 11 100); $\lambda_{\text{max}}^{\text{EtOH}+\text{AlCl}_3}$ (nm): 223, 252, 280, 321 (ϵ 15 100, 12 100, 9150, 8350. Gibbs test⁵ λ_{max} (nm): 430, 685 (Absorbance 0.14, 0.35). $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3270 (broad) 1649, 1603, 1578, 1291, 1156. MS: M, Found: 288.0630. Calc. for $\text{C}_{15}\text{H}_{12}\text{O}_6$: 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). $\lambda_{\text{max}}^{\text{EtOH}}$ (nm): 252, 292, 370 (ϵ 47 700, 17 050, 14 950). No alteration in presence of NaOAc. $\lambda_{\text{max}}^{\text{EtOH}+\text{NaOH}}$ (nm): 236, 276 (ϵ 42 900, 35 350). $\lambda_{\text{max}}^{\text{EtOH}+\text{AlCl}_3}$ (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). $\lambda_{\text{max}}^{\text{EtOH}}$ (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 reported² to contain friedelin, sitosterol, β -amyirin 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 Menzob, Caracas (1970).

² F. S. SILVA, *An. Acad. Brasil Cienc.* **40** (2), 155 (1968).