GUTTIFERAЕ

XANTHONES FROM KIELMEYERA RUBRIFLORA*†

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Abstract—Kielmeyera rubriflora Camb. contains 2-hydroxyxanthone, 2,4-dimethoxy-3-hydroxyxanthone, 2,3-dimethoxy-4-hydroxyxanthone, 4-hydroxy-2,3-methylenedioxyxanthone, 4-methoxy-2,3-methylenedioxyxanthone and 1,7-dimethoxy-2,3,8-trihydroxyxanthone (Ia).

Wood and bark of the tree Kielmeyera rubriflora Camb. (Guttiferae) were collected in the Sêrro region, Minas Gerais State, Brasil. The benzene extract of the wood yielded 2-hydroxyxanthone,1,2 2,4-dimethoxy-3-hydroxyxanthone,2 2,3-dimethoxy-4-hydroxyxanthone,2 4-hydroxy-2,3-methylenedioxyxanthone,2,3 4-methoxy-2,3-methylenedioxyxanthone,3,5 kielcorin4 and β-sitosterol. All the xanthones had been isolated previously from other Kielmeyera species and were identified by direct comparison with authentic samples.

The benzene extract of the bark yielded, besides aliphatic material, a new compound. Its molecular weight, determined by mass spectrometry, was consistent with the constitution of a dimethoxytrihydroxyxanthone. The PMR-spectrum confirmed the existence of two methoxyls and of three aromatic protons. One proton was represented by a singlet at 3.55~ and must, consequently, be placed at the 2-, 3- or 4-position of a trioxygenated ring. The remaining two protons were represented by doublets at 2.67~ (J 9.0 Hz) and 3.43~ (9.0 Hz) and must, consequently, be placed at the 5,6 or 6,7-positions of the dioxygenated ring. All signals were sufficiently up-field to preclude the existence of a proton at a peri (1,8)-position of either ring.6

One of these peri-positions is occupied by a hydroxyl, as shown by the shift of the UV absorption maxima upon addition of AlCl₃ + HCl. The second peri-position, however, is occupied by a methoxyl, since the compound reacted speedily with diazomethane to form a monohydroxy-tetramethoxyxanthone (and not a dihydroxy-trimethoxyxanthone). The mass spectrum of this derivative contained a peak corresponding to M-15-18 a.m.u. Loss of the elements of water upon electron impact again suggested the presence of a methoxy-group adjacent to the carbonyl.7

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The di-O-methyl derivative gave a Gibbs test maximum at 667 nm, typical of a system featuring an unsubstituted position, para related to a peri-hydroxyl. The Gibbs test, when performed on the original compound, as well as the shift of UV maxima upon addition of $\text{H}_2\text{BO}_3 + \text{NaOAc}$, indicated the presence of an ortho-dihydroxy grouping. Clearly, these hydroxyls cannot be situated at positions adjoining the peri-hydroxyl. Three vicinal hydroxy groups are incompatible with the relatively high stability of the compound in presence of alkali. They have, consequently, to be placed either at C-2, C-3 adjoining the peri-methoxyl, or at C-3, C-4. The latter alternative, however, cannot be correct, since it also would impart instability to a xanthone in alkaline medium. Thus, the peri-hydroxyl with the unsubstituted para-position is located in the disubstituted ring. In view of the vicinity of the hydrogens on this ring, the remaining methoxyl and the peri-hydroxyl must be ortho-related. This leads to the constitution of 1,7-dimethoxy-2,3,8-trihydroxyxanthone (Ia) for the new compound.

The 1,2,3,7,8-pentaoxygenation pattern has not been reported previously for a natural xanthone.

**EXPERIMENTAL**

For experimental techniques see Ref. 5. The identification of all previously described substances was confirmed by direct comparison (co-chromatography, mixed m.ps and IR spectra) with authentic samples.

Isolation of the constituents of Lielmeyera rubriflora. The powdered wood (7.0 kg) was continuously extracted with hot benzene. The filtered benzene solution was evaporated and the residue (18 g) was chromatographed on silica. Elution with CHCl$_3$ yielded, in order, 4-methoxy-2,3-methylenedioxyxanthone, $\beta$-sitosterol, 4-hydroxy-2,3-dimethoxyxanthone (20 mg), 3-hydroxy-2,3-dimethoxyxanthone (20 mg), 4-hydroxy-2,3-methylenedioxyxanthone (10 mg), 2-hydroxyxanthone (30 mg) and kielcorm (40 mg).

The powdered bark (7.0 kg) was continuously extracted with hot benzene. The filtered benzene solution was evaporated and the residue (35 g) was extracted exhaustively with light petroleum. The insoluble portion (8 g) was chromatographed on silica, yielding only aliphatic material which was not further examined. The light petroleum solution was filtered through silica and extracted with aqueous Na$_2$CO$_3$. The alkaline solution was acidified and extracted with CHCl$_3$. The CHCl$_3$ was evaporated and the residue was crystallized from MeOH, giving Ia (24 mg).

**1,7-Dimethoxy-2,3,8-trihydroxyxanthone (Ia).** Pale-yellow crystals, m.p. 198-200°; $\nu_{\text{max}}$ (cm$^{-1}$): 3300, 1635, 1612, 1580; $\lambda_{\text{max}}^{\text{EIOH NaOAc}}$ (nm): 231, 255, 281, 325, 394 (ε resp. 21,100, 20,050, 18,600, 11,300, 3800); $\lambda_{\text{max}}^{\text{EIOH NaOH HCl}}$ (nm): 237, 274, 368 (ε resp. 26,750, 14,900, 21,450); $\lambda_{\text{max}}^{\text{EIOH NaOH NaOAc}}$ (nm): 237, 289, 360 (ε resp. 26,500, 10,950, 15,050); $\lambda_{\text{max}}^{\text{EIOH NaOH HCl}}$ (nm): 255, 281, 324, 390 (ε resp. 20,500, 19,300, 10,850, 3500); $\lambda_{\text{max}}^{\text{EIOH NaOH HCl}}$ (nm): 256, 289, 355, 377 (ε resp. 16,200, 18,800, 10,200, 8500); $\lambda_{\text{max}}^{\text{HCl}}$ (nm): 256, 283, 330, 380 (ε resp. 15,950, 17,500, 10,200, 5400); $\lambda_{\text{max}}^{\text{HCl}}$ (nm): 237, 277, 368 (ε resp. 22,700, 14,200, 15,500). Gibbs test: $\lambda_{\text{max}}$ (nm): 460, 655 sh (Absorbance resp. 1.23, 0.37) NMR [(CD$_3$)$_2$CO, $\delta$]: $-1.27$ (s, OMe···O = C), 2.67 (d, J = 9 Hz, H-6), 3.43 (d, J = 9 Hz, H-5), 3.55 (s, 4-H), 6.18 (s, OCH$_3$), 6.23 (s, OCH$_3$); MS: M + 304 (100%), m/e (%): 289 (98), 286 (6), 274 (27), 271 (10), 261 (35), 246 (20), 152 (6), 123 (13).

8-Hydroxy-1,2,3,7-tetramethoxyxanthone (Ib). It was methylated with CH\textsubscript{2}N\textsubscript{2} in Et\textsubscript{2}O, yielding Ib as yellow crystals, m.p. 116–118°. \(\nu_{\text{max}}^{\text{KBr}}\) (cm\textsuperscript{-1}): 1658, 1608, 1593. \(\lambda_{\text{EiOH}}^{\text{max}}\) (nm): 236, 255, 280, 305, 368 (ε resp. 26,400, 34,900, 28,600, 19,700, 8600); no alteration upon addition of NaOAc and of H\textsubscript{2}BO\textsubscript{4} + NaOAc; \(\lambda_{\text{EiOH}+\text{NaOH}}^{\text{max}}\) (nm): 238, 277, 305 sh (ε resp. 43,500, 34,500, 12,800); acidification restored the spectrum in EtOH; \(\lambda_{\text{EiOH}+\text{AlCl}\textsubscript{3}}^{\text{max}}\) (nm): 234, 266, 280, 295 sh, 320, 335 sh (ε resp. 35,700, 24,900, 26,600, 22,000, 18,300, 14,900); \(\lambda_{\text{EiOH}+\text{AlCl}\textsubscript{3}+\text{HCl}}^{\text{max}}\) (nm): 225 sh, 233, 255 sh, 279, 295 sh, 335 sh, 394 (ε resp. 32,500, 34,600, 22,900, 29,700, 17,600, 11,600, 7400). Gibbs test\(^8\) \(\lambda_{\text{max}}\) (nm): 465, 685 (Absorbance resp. 0.35, 0.71); MS: M 332 (100%), \(m/e\) (\%) 327 (93), 302 (36), 299 (15), 287 (17), 274 (7), 259 (19).

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LEGUMINOSAE

ALIPHATIC ALCOHOLS, β-SITOSTEROLS AND ALKALOIDS IN

CASSIA JAHNII

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Plant. Cassia jahnii Britton & Rose. Leguminosae, known as Urumaco.

Source. Venezuelan Andes, at an altitude between 1500 and 3000 mts., near Mérida.

Use. Flowers used as purgative.

Previous work. Investigation of its anthraquinones.\(^1\)

Flowers. Alcoholic extract of flowers hydrolysed with aq. NaOH. The unsaponifiable material extracted with benzene and chromatographed on alumina with heptane. Initial fraction afforded a colourless solid m.p. 70–73°; TLC (Silica gel G, benzene) \(R_f\) 0·8; IR bands (KBr) \(\nu_{\text{max}}\) 3400, 2940, 2860, 1475, 1065, 725 cm\textsuperscript{-1}; NMR 6·4 \(\tau\) (1 H, OH), 8·79 \(\tau\) (5 H, CH\textsubscript{3}) and 9·02 \(\tau\) (3 H, CH\textsubscript{2}); thus, the product has the properties of an aliphatic straight chain, primary alcohol. The mass spectrum has a base peak at \(m/e\) 83 with other major peaks at \(m/e\) 97, 111, 139, 182, 196, 250, 294, 308, 336, 364 and 392. The four latter peaks have a relative abundance of 27, 50, 22 and 1% respectively. Since both the IR and NMR show the presence of a hydroxy group, these four peaks, in the above proportions, cannot be due to any one compound but rather to a mixture of four compounds having molecular ions of \(m/e\) 308, 336, 364 and 392. The absence of a \(M^+\)–18 peaks suggests that


\(^1\) C. SEELKOF and L. RUIZ TERÁN. Rev. Fac. Farm. Universidad de Los Andes 1, 7 (1958).