Phytochemistry, 1971, Vol. 10, pp. 2253 to 2255. Pergamon Press. Printed in England

GUTTIFERAE

XANTHONES FROM *KIELMEYERA RUBRIFLORA**†

O. R. GOTTLIEB, A. A. LINS MESQUITA and T. J. NAGEM
Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil

(*Received* 20 *October* 1970)

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,[2-5] 4-hydroxy-2,3-methylenedioxyxanthone,[2,3] 4-methoxy-2,3-methylenedioxyxanthone,[3,5] kielcorin[4] 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 3·55τ 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 τ (*J* 9·0 Hz) and 3·43 τ (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 $AlCl_3$ + 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]

* Part XXVII in the series "The Chemistry of Brazilian Guttiferae". For Part XXVI see Ref. 2.

† Taken, in part, from the M.Sc. Thesis submitted by T. J. Nagem to the Universidade Federal de Minas Gerais, Belo Horizonte (1970).

[1] O. R. GOTTLIEB and G. M. STEFANI, *Phytochem.* **9,** 453 (1970).
[2] O. R. GOTTLIEB, A. A. LINS MESQUITA, G. G. DE OLIVEIRA and M. TEIXEIRA DE MELO, *Phytochem.* **9,** 2537 (1970).
[3] O. R. GOTTLIEB, M. TAVEIRA MAGALHÃES, M. CAMEY, A. A. LINS MESQUITA and D. DE BARROS CORRÊA, *Tetrahedron* **22,** 1777 (1966).
[4] O. R. GOTTLIEB, A. A. LINS MESQUITA, E. MARTINS DA SILVA and M. TEIXEIRA DE MELO, *Phytochem.* **8,** 665 (1969).
[5] D. DE BARROS CORRÊA, L. G. FONSECA E SILVA, O. R. GOTTLIEB and S. JANOT GONÇALVES, *Phytochem.* **9,** 447 (1970).
[6] D. BARRACLOUGH, H. D. LOCKSLEY, F. SCHEINMANN, M. TAVEIRA MAGALHÃES and O. R. GOTTLIEB, *J. Chem. Soc.* (B), 603 (1970).
[7] J. H. BOWIE and P. Y. WHITE, *J. Chem. Soc.* (B), 89 (1969).

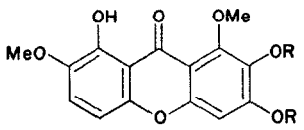
The di-*O*-methyl derivative gave a Gibbs test maximum at 667 nm, typical of a system featuring an unsubstituted position, *para* related to a *peri*-hydroxyl.[8] The Gibbs test,[8] when performed on the original compound, as well as the shift of UV maxima upon addition of H_3BO_3 + NaOAc, indicated 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.[8] 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, β-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 kielcorin (40 mg).



Ia R = H
b R = Me

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_2CO_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°; ν_{max}^{KBr} (cm^{-1}): 3350, 1635, 1612, 1580; λ_{max}^{EtOH} (nm): 231, 255, 281, 325, 394 (ε resp. 21,100, 20,050, 18,600, 11,300, 3800); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 237, 274, 368 (ε resp. 26,750, 14,900, 21,450); $\lambda_{max}^{EtOH+NaOH}$ (nm): 237, 289, 360 (ε resp. 26,500, 10,950, 15,050); $\lambda_{max}^{EtOH+NaOH\ HCl}$ (nm): 255, 281, 324, 390 (ε resp. 20,500, 19,300, 10,850, 3500); $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 256, 289, 335, 377 (ε resp 16,200, 18,800 10,200, 8500); $\lambda_{max}^{EtOH+AlCl+HCl}$ (nm): 256, 283, 330, 380 (ε resp. 15,950, 17,500, 10,200, 5400); $\lambda_{max}^{EtOH+H_3BO_3+NaOAc}$ (nm): 237, 277, 368 (ε resp. 22,700, 14,200, 15,500). Gibbs test[8] λ_{max} (nm): 460, 655 sh (Absorbance resp. 1·23, 0·37) NMR [$(CD_3)_2CO$, τ]: −1·27 (s, O<u>H</u> · · · O=C), 2·67 (d, *J* 9·0 Hz, H-6), 3·43 (d, *J* 9·0 Hz, 5-H), 3·55 (s, 4-H), 6·18 (s, OCH_3), 6·23 (s, $OC\underline{H}_3$); MS: M 304 (100%), *m/e* (%) 289 (98), 286 (6), 274 (27), 271 (10), 261 (35), 246 (20), 152 (6), 123 (13).

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

8-*Hydroxy*-1,2,3,7-*tetramethoxyxanthone* (Ib). Ia was methylated with CH_2N_2 in Et_2O, yielding Ib as yellow crystals, m.p. 116–118°. ν_{max}^{KBr} (cm^{-1}): 1658, 1608, 1593. λ_{max}^{EtOH} (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_3BO_3 + NaOAc; $\lambda_{max}^{EtOH+NaOH}$ (nm): 238, 277, 305 sh (ϵ resp. 43,500, 34,500, 12,800) acidification restored the spectrum in EtOH; $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 234, 266, 280, 295 sh, 320, 335 sh (ϵ resp. 35,700, 24,900, 26,600, 22,000, 18,300, 14,900); $\lambda_{max}^{EtOH+AlCl_3+HCl}$ (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] λ_{max} (nm): 465, 685 (Absorbance resp. 0·35, 0·71); MS: M 332 (100%), *m/e* (%) 317 (93), 302 (36), 299 (15), 287 (17), 274 (7), 259 (19).

Acknowledgements—The authors are indebted to the Conselho Nacional de Pesquisas, Brasil, for financial aid. They also want to thank Mr. A. Pereira Duarte, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil, for the collection and identification of the plant material, and Professor W. D. Ollis, The University, Sheffield, England, who kindly arranged for the determination of the mass spectra.

Phytochemistry, 1971, Vol. 10, pp. 2255 to 2256. Pergamon Press. Printed in England.

LEGUMINOSAE

ALIPHATIC ALCOHOLS, β-SITOSTEROLS AND ALKALOIDS IN *CASSIA JAHNII*

A. MORALES MENDEZ*

Instituto de Investigaciones Químicas. Facultad de Farmacia, Universidad de Los Andes, Mérida, Venezuela

(*Received* 16 *November* 1970)

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) ν_{max} 3400, 2940, 2860, 1475, 1065, 725 cm^{-1}; NMR 6·4 τ (1 H, OH), 8·79 τ (50 H, CH_2) and 9·02 τ (3 H, CH_3): 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

* Present address. Departamento de Química. Universidad Metropolitana. Avda. Gamboa San Bernardino, Caracas.

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