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XANTHONES FROM *KIELMEYERA EXCELSA*[1]

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Abstract—2-Hydroxyxanthone, 1,7-dihydroxyxanthone, 1-hydroxy-7-methoxyxanthone, 2-hydroxy-1-methoxyxanthone, 1,2-methylenedioxyxanthone and 2,8-dihydroxy-1-methoxyxanthone were isolated from the wood of *Kielmeyera excelsa* Camb.

THE WOOD of *Kielmeyera excelsa* Camb. was found to contain 2-hydroxyxanthone, 1,7-dihydroxyxanthone (euxanthone), 1-hydroxy-7-methoxyxanthone, 2-hydroxy-1-methoxyxanthone and 2,8-dihydroxy-1-methoxyxanthone. All these compounds had already been isolated previously from other species of the same genus[2] and were identified by direct comparison with authentic samples. Only one constituent proved to be a new natural compound. The molecular weight, determined by mass spectrometry, fitted a methylenedioxyxanthone structure. Besides the molecular ion peak, this spectrum contained only one more intense peak at M-1 mass units. The ease with which the molecule loses a hydrogen atom was also indicative of a methylenedioxy–benzene system which aromatizes upon electron impact. Of the three possible methylenedioxyxanthones, only the 1,2-derivative was given consideration, in view of its probable biosynthetic relationship to 2-hydroxy-1-methoxyxanthone. Indeed, treatment of the natural isolate with PCl_5 and hydrolysis of the reaction product[3] yielded 1,2-dihydroxyxanthone.

1,2-Methylenedioxyxanthone, which has been synthesized,[4] is the fourth natural methylenedioxyxanthone to be reported. Other representatives of this relatively small group include 4-hydroxy-2,3-methylenedioxyxanthone, 4-methoxy-2,3-methylenedioxyxanthone[5] and 1,2,4-trimethoxy-6,7-methylenedioxyxanthone.[6]

1,2-Oxygenation of a xanthone ring is not common among *Kielmeyera* constituents. Up to now, the only principal metabolites to be characterized by this structural feature were found to occur in *K. petiolaris* (Spr.) Mart.[7] Within the Guttiferae family, *K. excelsa* and *K. petiolaris* form a pair of vicarious species,[8] stemming from a common ancestor, but thriving presently in contiguous, but different ecological environment. *K. excelsa* is found

[1] Part XIX in the series "The Chemistry of Brazilian Guttiferae"; for part XVIII see D. DE BARROS CORRÊA, L. G. FONSECA E SILVA, O. R. GOTTLIEB and S. JANOT GONÇALVES, *Phytochem.* 9, 447 (1970).
[2] For ref. to the original lit. see O. R. GOTTLIEB, *Phytochem.* 7, 411 (1968).
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in the humid tropical forest of the Atlantic coast, while *K. petiolaris* grows in the dry savannah-like region of central Brazil. The similarity in oxygenation pattern of the xanthonic constituents of these species is, consequently, paralleled by their morphological and phylogenetic affinity.

EXPERIMENTAL

For experimental techniques see the preceding paper of this series.[1] The identification of all substances was confirmed by direct comparison (co-chromatography, mixture m.p., u.v. and i.r. spectra) with authentic samples.

Benzene extraction of the sapwood of Kielmeyera excelsa. *Isolation of euxanthone, 2-hydroxyxanthone, 1-hydroxy-7-methoxyxanthone, 1,2-methylenedioxyxanthone, β-sitosterol, 2,8-dihydroxy-1-methoxyxanthone and 2-hydroxy-1-methoxyxanthone.* The powdered wood (12 kg) was continuously extracted with hot benzene. Removal of the benzene gave a residue (47·5 g) which was taken up with a small volume of benzene. An insoluble crystalline mass (2·1 g) which appeared was separated by filtration from the benzene solution and chromatographed on silica (50 g) giving various fractions with the indicated solvents: benzene (A_1), benzene–$CHCl_3$, 2:1 (A_2), benzene–$CHCl_3$, 1:2 (A_3). The benzene solution was evaporated to dryness and the residue (45·0 g) was chromatographed on silica (900 g) giving various fraction with the indicated solvents: benzene (B_1), $CHCl_3$ and $CHCl_3$–MeOH, 99:1 (B_2), $CHCl_3$–MeOH, 99:2 (B_3, B_4, B_5 in this order).

A_1 was recrystallized from benzene–EtOH yielding an aliphatic aldehyde (25 mg), m.p. 83–87°, ν_{max}^{KBr} 2912, 2830, 1738, 1600, 1460, 1175, 730, 720 cm^{-1}, which was not further examined. A_2 was recrystallized from EtOH yielding euxanthone (20 mg). A_3 (0·2 g) was rechromatographed on silica to separate an additional small quantity of euxanthone from a fraction which, upon crystallization from ethanol, yielded 2-hydroxyxanthone (43 mg). B_1 (1·3 g) was crystallized from light petroleum–benzene yielding 1-hydroxy-7-methoxyxanthone (100 mg). B_2 (0·5 g) was subjected to fractional crystallizations from ethyl acetate. Initial crops: 1,2-methylenedioxyxanthone (16 mg). Last crops: aliphatic alcohol (5 mg), m.p. 82–84°, ν_{max}^{KBr} 3400, 2930, 2860, 1475, 1050, 725 cm^{-1}, which was not further examined. B_3 (2 g) was submitted to fractional crystallization from acetone. Initial crops: β-sitosterol (171 mg). Last crops: 1,2-methylenedioxyxanthone (190 mg). B_4 (15 g) was washed with light petroleum. From the insoluble part nothing useful could be isolated. The soluble part (0·2 g) was separated by thick layer chromatography (silica, $CHCl_3$–acetone, 95:5) into 2,8-dihydroxy-1-methoxyxanthone (94 mg, after recrystallization from $CHCl_3$), 1-methoxy-2-hydroxyxanthone (19 mg, after recrystallization from light petroleum–benzene), euxanthone and 2-hydroxyxanthone (small quantities), quoted in order of decreasing R_f. B_5 (2·9 g) was freed from resin by filtration through silica and recrystallized from ethyl acetate yielding an aliphatic compound, m.p. 87–88°, ν_{max}^{KBr} 2930, 2860, 1713, 1460 cm^{-1}, which was not further examined.

Euxanthone. Found: m.p. 236–237°. Required: m.p. 236–237°.[9] *2-Hydroxyxanthone.* Found: m.p. 238–239°. M 212. Required: m.p. 240–242°,[10] M 212. *1-Hydroxy-7-methoxyxanthone.* Found: m.p. 130–131°. Required: m.p. 129–131°.[11] *β-Sitosterol.* Found: m.p. 139–141°. Required: m.p. 136–138°. *2,8-Dihydroxy-1-methoxyxanthone.* Found: m.p. 199–201°. Required: 197–199°.[7] *2-Hydroxy-1-methoxyxanthone.* Found: 171–173°. Required: 169–171°.[4]

1,2-Methylenedioxyxanthone. Colourless crystals, m.p. 217–218° (lit.[4] 212°). λ_{max}^{EtOH} 246, 270 sh., 308, 353 nm (ε resp. 45,500, 10,600, 18,000, 14,000); no alteration in presence of NaOH, NaOAc, $AlCl_3$. ν_{max}^{KBr} 1650, 1476, 1456, 1313, 1253, 1225, 1191, 1150, 1141, 1116, 1019, 928, 922, 872, 853, 834, 772, 744, 694, 691, 631 cm^{-1}. Mass spectrum: *m/e* (%) 241 (16), 240 (100), 239 (42).

Hydrolysis of 1,2-methylenedioxyxanthone. 1,2-Methylenedioxyxanthone (150 mg) and PCl_5 (1·5 g) in xylene (10 ml) were heated under reflux (3 hr). The xylene was removed by entrainment with water vapour. The residual mixture was cooled to room temperature and extracted with $CHCl_3$. The extract was washed to neutrality, dried and evaporated. The brown residue was chromatographed on a dry column (silica deactivated with water, developing mixture benzene–ethyl acetate–ethanol, 72:25:3) yielding a crystalline fraction. Recrystallization from EtOH led to a small quantity of 1,2-dihydroxyxanthone, m.p. 165–167° (lit.[4] 165–167°), identified by direct comparison with an authentic sample.

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