Notas & Comunicações

The Chemistry of Brazilian Guttiferae. XXXVI. Constituents of amazonian species

Sonia J. Gabriel (1), Otto R. Gottlieb (2), Roberto A. de Lima (3) e Antonio A. L. Mesquita (4)

In continuation of a series of reports on the chemical composition of Guttiferae, belonging predominantly to the genus *Kielmeyera* from central Brazil (Castelão Jr. *et. al.*, 1977), we examined the following species from the Amazon region.

Caraipa costata Spruce ex Benth.

A trunk wood sample from the vicinity of Manaus was freed from bark, ground and extracted with benzene. The extract (8%, 41g) was chromatographed on a silica column, giving successively the following useful fractions with the indicated solvents: A_1 and A_2 (benzene-EtOH 98:2), A_3 and A_4 (benzene-EtOH 96:4), A_5 and A_6 (benzene-EtOH 94:6). A_1 was rechromatographed on florisil giving a red band which, extruded and extracted with $CHCl_3$, gave physcion (1,8-dihydroxy-6-methoxy-3-methylanthraquinone, 5 mg), m.p. and lit. [Eder & Hauser, 1925] m.p. 205-207°. A_2 was freed from oil by chromatography on silica giving lichexanthone (1-hydroxy-3,6-dimethoxy-8-methylxanthone, 6 mg) m.p. and lit. [Roberts, 1961] m.p. 186-187°. A_3 was chromatographed on a dry silica column giving aliphatic ester (70 mg), lichexanthone (5 mg) and lupenone (50 mg).

---

(1) — Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, Itaguaí.
(2) — Instituto de Química, Universidade de São Paulo, São Paulo.
(3) — Departamento de Química, Universidade Federal de Alagoas, Maceió.
(4) — Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte.

Caraipa grandifolia Mart.

Previous work on this species revealed the presence of sitosterol, lupeol, lupenone, betulinic acid and vanilin [Lima *et al.*, 1972]. The present work concerned again a trunk wood sample from the estuary of the Amazon river. This was ground and extracted with benzene. The extract (5%, 18g) was chromatographed on silica. The benzene-EtOH 97:3 eluate was dissolved in hot EtOH. Upon cooling to O° betulinic acid (3 g) precipitated and was removed by filtration. The solvent was evaporated and the residue, in Et_2O, extracted successively with aq. Na_2CO_3 and NaOH. The Na_2CO_3 solubles were precipitated with HCl and filtered through silica to give 4-hydroxy-2,3-dimethoxyxanthone (6 mg), m. p. and lit. [Gottlieb *et al.*, 1966] m.p. 218-219°. The NaOH solubles were precipitated with HCl and crystallized from EtOH to give cadensin-A (2 mg) [Castelão Jr. *et al.*, 1977]. In the mother liquor 1,5-dihydroxy-6,7-dimethoxyxanthone [Lima *et al.*, 1972] was detected by TLC. The neutral fraction was crystallized from EtOH giving betulin (300 mg).

Caraipa psidifolia Ducke

The benzene extract of a trunk wood sample from the IPEAN Forest Reserve, Belém, IPEAN N.° 184-40-53, wood collection U. of Brasília N.° 63, examined by TLC, was shown to contain sitosterol, lupeol, 2-methoxyxanthone [Pimenta et al., 1964] and 1,5-dihydroxy-6,7-dimethoxyxanthone.

Caraipa valioi Paula [Paula, 1970, 1976]

A trunk wood sample from the Ducke Forest Reserve, Manaus, was extracted with light petroleum. The extract, examined by preparative TLC, was shown to contain sitosterol, lupeol, betulinic acid, aliphatic ester, 1,5-dihydroxy-6,7-dimethoxyxanthone and cadensin-A.

Haploclathra verticillata Ducke

A trunk wood sample from Amazonas State, voucher Herbarium RB 29035, was extracted with benzene. The extract, examined by silica TLC, was shown to contain sitosterol, lupeol, betulinic acid, 1,7-dihydroxyxanthone and 1-hydroxy-7-methoxyxanthone [Gottlieb & Stefani, 1970].

Mahurea tomentosa Ducke

A trunk wood sample from Amazonas State, voucher RB 23779, was extracted with benzene. The extract, fractionated by preparative silica TLC, gave sitosterol, 1-7-dihydroxyxanthone and 1-hydroxy-7-methoxyxanthone.

Platonia insignis Mart.

A trunk wood sample of "bacurí", from the vicinity of Manaus, was extracted with ethanol. The extract yielded by crystallization 1,7-dihydroxyxanthone (euxanthone), first isolated from this source by Spoelstra and van Royen, 1929. The mother liquor was extracted with aqueous borax. The product obtained by acidification of the aqueous solution was fractionally crystallized from methanol to give successively a 1,6-dihydroxy-7-0-glycosylxanthone, yellow crystals, 300° dec., and 1,6,7-thihydroxyxanthone, m.p. and m.m.p. with an authentic sample, contributed by Dr. F. Scheinmann, 278-280° [Carpenter *et al.*, 1969]. The heteroside was cleaved by acid hydrolysis into an unidentified sugar and 1,6,7-trihydroxyxanthone. The location of the glycosyl was established by UV (shifts of maxima occurred upon addition of $AlCl_3+HCl$ and NaOAc).

COMMENTS

The genera *Caraipa* and *Kielmeyera* belong to different tribes of the subfamily Kielmeyeroideae [Melchior, 1964]. The structural similarity of their xanthones is, thus, not surprising. A chemical difference indicated by the present work refers to the relative quantity of xanthonse (which predominate in *Kielmeyera*) vs. triterpenoids of the lupane class (which predominate in *Caraipa*).

The presence of lichexanthone and physcion in *C. costata* seems to indicate the co-extraction of a lichen. It should be noted, however, that the analysed wood sample was freed from bark prior to extraction.

ACKNOWLEDGEMENT

Plant material was classified by Dr. José Elias de Paula, Universidade de Brasília.

LITERATURE CITED

Carpenter, I.; Locksley, H.D. & Scheinmann, F.
1969 — The structure of seven xanthones from the heartwood of **Mammea africana** L. **J. Chem. Soc.** (C) 2421-2425.

Castelão Jr., J.F.; Gottlieb, O.R.; Lima, R.A. de; Mesquita, A.A.L.; Gottlieb, H.E. & Wenkert, E.
1977 — The chemistry of Brazilian Guttiferae. XXXV. Xanthonolignoids from **Kielmeyera** and **Caraipa** species. ^{13}C NMR spectroscopy of xanthones. **Phytochemistry** 16 : no prelo.

Eder, R. & Hauser, F.
1925 — Über den natürlich vorkommenden Frangula-Emodinmonomethyläther. **Helv. Chim. Acta,** 8 : 140-145.

Gottlieb, O. R. Magalhães, M.T.; Camey, M.; Mesquita, A.A.L. & Corrêa, D. de B.
1966 — The chemistry of Brazilian Guttiferae. V. 2,3,4- and 1,3,5-trioxygenated xanthones from **Kielmeyera** species. **Tetrahedron,** 22 : 1777-1784.

Gottlieb, O.R. & Stefani, G.M.
1970 — The chemistry of Brazilian Guttiferae. XIX. Xanthones from **Kielmeyera excelsa. Phytochemistry**, 9(2):453-454.

Lima, R.A. de; Gottlieb, O.R. & Mesquita, A.A.L.
1972 — The chemistry of Brazilian Guttiferae. XXVIII. Xanthones from **Caraipa densiflora. Phytochemistry**, 11(7):2307-2309.

Melchior, H.
1964 — A. Engler's Syllabus der Pflanzenfamilien, 12. Ed., vol. II, Gebrüder Bornträger, Berlin.

Paula, J.E. de
1970 — Guttiferae novas da Amazônia. **Ciência e Cultura,** 22(4) : 369-378.
1976 — Anatomia de **Lorostemon coelhoi** Paula, **Caraipa valioi** Paula e **Clusia** aff. **macrcpoda** Klotsch (Guttiferae da Amazônia). **Acta Amazonica,** 6(3) : 273-291.

Pimenta, A.; Mesquita, A.A.L.; Camey, M.; Gottlieb, O.R. & Magalhães, M.T.
1964 — A química das gutíferas Brasileiras. I. Constituintes xantônicos da **Kielmeyera coriacea. An. Acad. Brasil. Ciênc.** 36(1): 39-41.

Roberts, J.C.
1961 — Naturally occurring xanthones. **Chem. Rev.,** 61 : 591-605.

Spoelstra, D.B. & Royen, M.J. Van
1929 — Notiz über das Vorkommen von Euxanthon im Kernholze von **Platonia insignis** Mart. ("Geelhart" oder "Pakoeli") **Rec. trav. chim. Pays-Bas** 48 : 370-371.