

## XANTHOCHYMOL FROM *CLUSIA ROSEA* (GUTTIFERAE)

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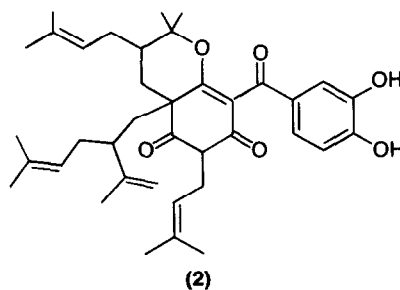
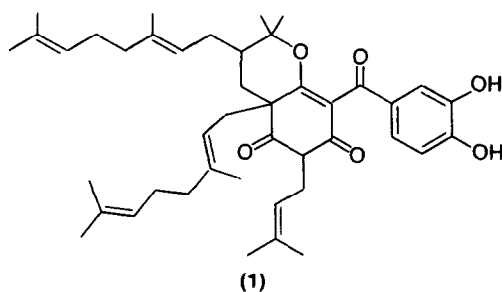
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**Key Word Index**—*Clusia rosea*, Guttiferae, xanthochymol, complex hexaprenyl phenol

The mature fruit of the Autograph Tree (*Clusia rosea* Jacq)<sup>1</sup> contains a yellow resin. The isolation of a number of triterpenes from the Autograph Tree has previously been reported.<sup>2</sup> This paper describes work on the isolation and identification of the pigment in this resin.

The fruit was ground, extracted with benzene and the pigments isolated from the extracts by column chromatography. The yellow pigment, m.p. 130–132°, slowly crystallized from these fractions rich in the pigments. It gave a black ferric chloride test. The IR spectrum showed a broad band at 3300 and carbonyl bands at 1745 and 1655 as well as a strong band at 1630  $\text{cm}^{-1}$ . The UV spectrum was essentially identical with that of bromianone (1)<sup>3,4</sup> suggesting identical chromophones in each case. The UV spectrum changed with added base confirming the presence of phenolic hydroxy groups consistent with the positive  $\text{FeCl}_3$  test.

The mass spectrum gave a molecular ion at  $m/e$  602 which showed that the yellow *Clusia* pigment was not identical with bromianone (1). The mass spectrum of the *Clusia* pigment showed strong M-69 (isopentenyl) and M-137 peaks. However, the latter fragment, M-137, could be assigned to either M-C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>(3,4-dihydroxybenzoyl) or M-C<sub>10</sub>H<sub>17</sub>(geranyl).



The NMR spectrum was complex and among other groups indicated the presence of isoprenoid side chains attached to an aromatic system. The NMR spectrum showed signals for: (a) three aromatic protons; (b) three vinyl protons; (c) a  $\text{C}=\text{CH}_2$  group; and (d)

<sup>1</sup> NIAL, M. C. (1965) In *Gardens of Hawaii* Bishop Museum Press, Honolulu, p. 586. HARGREAVES, D., and HARGREAVES, B. (1964) *Tropical Trees of Hawaii*, p. 3, Hargreaves, Kailua

<sup>2</sup> MATHUR, S. B. (1972) *Phytochemistry* **11**, 1513

<sup>3</sup> OLLIS, W. D., REDMAN, B. T., SUTHERLAND, I. O. and JEWERS, K. (1969) *Chem. Commun.* 879, OLLIS, W. D. (1970) *An Acad. Brasil. Cienc.* **42**, 9

<sup>4</sup> RAMA RAO, A. V., VENKATARAMAN, K. and YEMUL, S. S. (1973) *Tetrahedron Letters* 4981

an uncertain number of vinyl C-methyls. There was complex adsorption in the region  $\delta$  1.8–2.8 which was obviously due to many overlapping signals.

At this juncture it became apparent that the yellow pigment was probably identical with xanthochymol (2) isolated from *Garcinia xanthochymus* (Guttiferae).<sup>5</sup> Proof of identity was obtained by direct comparison with an authentic sample of 2.

#### EXPERIMENTAL

**Isolation.** Fruit of *C. rosea* was collected from street trees along Aupuni St. in Hilo, Hawaii, August 1971. The dried fruit was ground and extracted with benzene. Solvent was removed from the extracts and the residue chromatographed on silicic acid. Lipids and other non-polar materials were eluted with hexane. Benzene eluted the yellow pigment along with further oils. Solvent was removed from those benzene fractions which showed a black  $\text{FeCl}_3$  test and the residue allowed to stand with hexane whereupon yellow hair-like crystals slowly formed, m.p. 130–132°.  $\lambda_{\text{max}}^{\text{EtOH}}$  252, ~275, 362 nm;  $\lambda_{\text{max}}^{\text{EtOH-NaOH}}$  287, 402 nm;  $\nu$  3300 (hydroxy), 1745, 1655 (carbonyl)  $\text{cm}^{-1}$  (Nujol); NMR  $\delta$  6.92 (d, 2H, aromatic), 6.54 (d, 1H, aromatic), 4.96 (m, 3H, vinyl), 4.61, 4.41 (2H, C-CH<sub>2</sub>) ( $\text{CDCl}_3$ ); MS *m/z* (relative intensity) 662 (30), 574 (7), 533 (3), 467 (8), 466 (37), 465 (100), 464 (6), 449 (6), 410 (6), 341 (22), 231 (20), 187 (6), 177 (7), 137 (37), 110 (7), 109 (7), 95 (10), 91 (6), 81 (10), 69 (60), 55 (8), 41 (37). Found: C, 74.1, H, 8.48.  $\text{C}_{34}\text{H}_{40}\text{O}_6$  requires: C, 75.01, H, 8.30%.

Crude plant extracts which were not worked up promptly and had stood at RT for some months could not be made to yield crystalline material after eventual work-up.

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<sup>5</sup> KARANIGOUKAR, C. G., RAMA RAO, A. V., VENKATARAMAN, K. and PATIL, K. P. (1973) *Tetrahedron Letters* 4977.

Xanthochymol: 1973, Vol. 14, pp. 3243–3247, Pergamon Press, Oxford and Elsevier.

### O-METHYLFLAVINANTINE FROM *RHIGIOCARYA RACEMIFERA*\*

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**Plant.** *Rhigiocarya racemifera* Miers (Menispermaceae). **Source.** Ghana, West Africa (a voucher specimen is on deposit at the Faculty of Pharmacy, University of Science and Technology, Kumasi, Ghana, West Africa). **Uses.** Medicinally,<sup>1</sup> the powdered leaves and juice for nasal drops and the leafy twigs, roots and seeds as an aphrodisiac.

\* Part IV in the Series Constituents of West African Medicinal Plants. For Part III see Tackie, A. N., Dwuma-Badu, D., Lartey, P. A., Schiff, Jr., P. L., Knapp, J. E. and Slatkin, D. J. (1974) *Lloydia* 37, 6.

<sup>1</sup> Irvine, E. R. (1961) *Wooded Plants of Ghana*, p. 77, Oxford University Press, London.