QUINONES AND OTHER CONSTITUENTS OF *MARKHAMIA PLATYCALYX* AND *BIGNONIA UNGUISCATI*

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In pursuing our interest (1) in quinone constituents of the Bignoniaceae, we have chemically examined *Markhamia platycalyx* Sprague (Syn: *Dolichandrone platycalyx*) and *Bignonia unquiscati* Rehd. (Syn: *Doxantha unguis* Miers.) and described the isolation of lapachol, β-lapachone, dehydro-iso-α-lapachone, *d*-sesamin, paulownin, and stigmasterol from the C_6H_6 extract of the heartwood of *M. platycalyx*. Extraction of the aerial parts of *B. unguiscati* with petroleum ether afforded lapachol, ceryl alcohol, β-amyrin, and β-sitosterol. In view of the observations that lapachol exhibits potent antitumor activity (2) and that β-lapachone is a potent inhibitor of reverse transcriptase activity as well as showing eukaryotic DNA-dependent DNA-polymerase activity (3), it was thought that a phytochemical examination of these plants would be interesting.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded with the following instruments: ir, Perkin-Elmer model 577; uv, Pye Unichem SP-8100; nmr, Perkin-Elmer R 12B 60 Hz; ms, Hitachi model RMU 6E. Melting points were determined in soft glass capillaries in an electrothermal mp apparatus. Thin layer chromatographs were conducted on Merck's Kieselgel G; in chromatographic fractionations Brockmann alumina was used and 2% ceric sulphate in 2N H_2SO_4 was the spray regent used in tlc.

PLANT MATERIALS.—The heartwood of *M. platycalyx* was collected from Forest Research Institute, Dehradun, India, and a voucher specimen was deposited in the FRI Herbarium, Dehradun. Aerial parts of *B. unguiscati* were obtained from United Chemicals and Allied Products, Clive Row-10, Calcutta, and a voucher specimen was deposited in UCAP, Calcutta.

EXTRACTION AND ISOLATION.—Air-dried and coarsely powdered heartwood (1 kg) of *M. platycalyx* was exhaustively extracted with C_6H_6 (3 × 12 h). The extract was concentrated to dryness in vacuum. It was taken up in Et_2O and then extracted with 2N Na_2CO_3. The alkali-soluble fraction was acidified with 2N HCl. The yellow mass obtained on acidification was chromatographed over silica gel giving lapachol (50 mg). The ethereal fraction containing neutral components was chromatographed over deactivated alumina and afforded β-lapachone (20 mg), dehydro-iso-α-lapachone (15 mg), *d*-sesamin (15 mg), paulownin (10 mg), and stigmasterol (15 mg). The coarsely powdered air-dried aerial parts (1 kg) of *B. unguiscati* were completely extracted with petroleum ether (60-80°) and worked up as described above. The alkali soluble fraction was acidified with 2N HCl and the precipitate chromatographed over silica gel, giving lapachol (40 mg). The neutral ether fraction was chromatographed over deactivated alumina and gave ceryl alcohol (10 mg), β-amyrin (20 mg), and β-sitosterol (10 mg).

All quinonoid and lignan constituents were identified by standard spectral data as well as by comparison with authentic samples and color reactions (4-6). The structure of β-lapachone was further confirmed by its conversion to α-lapachone with HCl, and that of paulownin was clarified by preparation of its methanolate, mp 84-85°.

Full details of the isolation and identification of the compounds are available on request to the senior author.

ACKNOWLEDGMENTS

The authors wish to thank the Council of Scientific and Industrial Research, New Delhi, for the award of Junior Research Fellowship to one of us (MCS).

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Received 17 January 1984