

Isolation of compound 2. The essential oil was chromatographed on HPLC using a 50×0.8 cm LiChrosorb SI 60 (Merck) column. The eluant was MeCOMe- C_6H_6 (2:8), at a flow rate of 145 ml/hr. A Pye LCM2 hot wire detector was used. The fractions which contained a substance eluted at retention time 13 min were combined. After evaporation of the solvent a crystalline substance was obtained (19.5 mg). Recrystallization from MeCOMe- C_6H_6 gave colourless platelets, mp 139–140.5°. High resolution MS, m/e 246 (M^+) $C_{14}H_{14}O_4$. (Found: 246.0887, Calc. for 246.0890). High resolution MS of the TMSi derivative m/e 390 (M^+) $C_{20}H_{30}O_4Si_2$. (Found: 390.1679, Calcd.: 390.1680).

Cyclization of 2. Cyclization of compound 2 was carried out by the same methods described above to give xanthyletin (6.0 mg) (mp 130.8–131.8°).

Cyclization of 1 and 2 with $ZnCl_2$. Each of 1 (0.23 mg) and 2 (0.23 mg) was suspended in C_6H_6 (2 ml) and $ZnCl_2$ (4 mg) was added, and the mixture was stirred at room temp. An aliquot (50 μ l) of the organic layer was taken out every 10 min and chromatographed on HPLC using a 30×0.3 cm LiChrosorb SI 60 (Merck) column with EtOAc- C_6H_6 (5:95) as an eluant, at a flow rate of 35 ml/hr. CECIL CE212 (UV 348 nm) was used as a detector. The retention time of xanthyletin was 5.15 min. The quantity of the product was estimated from the peak height and the calibration curve given by authentic xanthyletin.

Isolation of bergapten, chalepensis and xanthyletin. Leaving the essential oil in a refrigerator for a month, after the removal of 1, gave bergapten (11.4 mg). Recrystallization from EtOH gave white needles, mp 187.5–189°. On HPLC of the residual essential oil, hexane eluates afforded chalepensis (110 mg). It was recrystallized from EtOH- H_2O mp 87.9–88.2°. The subse-

quent fractions eluted with C_6H_6 yielded xanthyletin (54.4 mg). It was recrystallized from C_6H_6 -hexane mp 131–132°.

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REFERENCES

- Ohta, T. and Miyazaki, T. (1958) *Yakugaku Zasshi* 78, 1067; (1959) *Chem. Abstr.* 53, 1636a.
- Miyazaki, T. and Mihashi, S. (1964) *Chem. Pharm. Bull.* (Tokyo) 12, 1232; (1965) *Chem. Abstr.* 62, 2755g.
- Talapatra, S. K., Mukhopadhyay, S. K. and Talapatra, B. (1973) *Phytochemistry* 12, 2312.
- Nayar, M. N. S., Bhan, M. K. and George, V. (1973) *Phytochemistry* 12, 2073.
- Bahn, M. K., Raj, S., Nayar, M. N. S. and Handa, K. L. (1973) *Phytochemistry* 12, 3010.
- Kozawa, M., Baba, K., Minami, M., Nitta, H. and Hata, K. (1974) *Chem. Pharm. Bull.* 22, 2746; (1975) *Chem. Abstr.* 82, 95297g.
- Talapatra, S. K., Mukhopadhyay, S. K. and Talapatra, B. (1975) *Phytochemistry* 14, 836.
- Deniges, G., (1898) *Compt. Rend.* 126, 1145, 1277.
- Pierce, A. E. (1968) 'Silylation of Organic Compounds' p. 23, Pierce Chemical Company, Rockford, Illinois.
- Rangaswami, S. and Seshadri, T. R. (1940) *Proc. Indian Acad. Sci.* 12A, 375; (1941) *Chem. Abstr.* 35, 3526.
- Morita, N. and Shimizu, M. (1966) *Yakugaku Zasshi* 86, 732; (1966) *Chem. Abstr.* 65, 17365c.

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A PRENYLATED CHALKONE FROM *MILLETIA OVALIFOLIA*

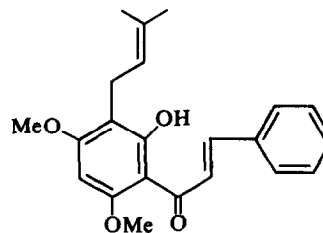
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Key Word Index—*Milletia ovalifolia*; Leguminosae; A new prenylated chalkone; ovalichalkone; 2'-hydroxy-3'-C-prenyl-4',6'-dimethoxy chalkone).

In continuation of our earlier work [1], further examination of the seeds of *Milletia ovalifolia* led to the isolation of an additional chalkone designated as ovalichalkone. It was assigned structure (1) based on spectral and synthetic evidence. mp 123–24° yellow needles, molecular formula $C_{22}H_{24}O_4$ M^+ (352), +ve Gibbs test. λ_{max}^{MeOH} nm 345 (log ϵ 4.49). IR ν_{max}^{KBr} : 1630, 1580, 1470, 1410, 1330, 1220, 1120, 980, 780 cm^{-1} . PMR (δ values solvent $CDCl_3$): gem dimethyl allyl group is shown by the following peaks. 1.8(d, 6H, $J = 6$ Hz, $CH_3)_2C=$); 3.35 (m, 2H, $-CH_2-CH=C=$); 5.4 (m, 1H, $-CH=C(Me)_2$). Two methoxyl groups shown by peaks at 4.0 (s, 3H, $-OMe$) and 3.95 (s, 3H, $-OMe$); aromatic protons and α , β -protons are shown by peaks at 6.1 (s, 1H, H-5'); 7.55 (m, 5H, H-2, 3, 4, 5, 6); 7.95 (s, 2H, H- α , β); chelated hydroxyl at 14.6 (s, 1H, $-OH$ at 2') (D_2O exchangeable). The mass fragments at 337 (99%) (M-15); 321 (14.3) (M-31); 309 (99) (M-43); 297 (85.3) M-55; 275 (25.3) (M-77) and at 248 (14.3) (M-104=a); 233 (98) (a-15); 205 (77) (a-43); 193 (99) (M-55-104); 131 (44) (cinnamoyl); 103 (66), agreeing with the structure 1 for ovalichalkone. This was confirmed by synthesis from 5-C-prenyl-2,4-di-O-methyl-phloracetophenone mp 113–114° (lit. [2] mp 113°C); UV λ_{max}^{MeOH} nm 290 (log ϵ 4.33). IR ν_{max}^{KBr} : 1620, 1590, 1460, 1415, 1380, 1360, 1230, 1180, 1130, 890 cm^{-1} . PMR (δ values solvent $CDCl_3$);



1.7 (d, 6H, $J = 6$ Hz $(CH_3)_2C=$); 2.6 (s, 3H, $-COCH_3$); 3.3 (m, 2H $-CH_2-CH=C(Me)_2$); 3.9 (s, 6H, 2 $-OMe$); 5.2 (m, 1H, $-CH_2-CH=C(Me)_2$); 6.0 (s, 1H, H-3); 14.4 (s, 1H, chelated $-OH$). The above ketone on condensation with benzaldehyde under alkaline conditions yielded a chalkone which was identical with the natural sample (co-TLC, mmp and co-IR spectra in KBr).

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REFERENCES

- Gupta, R. K. and Krishnamurti, M. (1976) 15, 832.
- Vandewalle, M. (1961) *Bull. Soc. Chim. Belg.* 70, 163; Jain, A. C. and Zutshi, M. K. (1971) *Tetrahedron Letters* 34, 3179.