limonene, 1,8-cineol and *p*-cymene in the volatile oil and ether extracts from this material.

The ether extracts (20 ml) of the seeds (3 kg) were chromatographed on $Si_2O$ with hexane–$C_6H_6$ mixtures (19:1–1:19) and $C_6H_6$ and analysed by TLC (Si gel GF (Merk), $C_6H_6$). The positive fractions with Brady's reagent were rechromatographed with $C_6H_6$ to give similar smelling, pale yellow oils **1** (25 mg) and **2** (20 mg). Analytical samples were obtained by prep TLC (Si gel GF (Merck), hexane). These compounds analysed for $C_{10}H_{10}O$. $M^+ = 146$ and preliminary investigation showed the presence of a CHO.

**1** formed a 2,4-dinitrophenylhydrazone, orange needles, mp 253–254°, $C_{10}H_{14}N_4O_4$, $M^+ = 326.1006$. IR of **1** showed absorption at 1692 $cm^{-1}$ due to the aromatic aldehyde. The PMR (60 M Hz) in $CCl_4$ showed signals at $\delta$ 2.19 (2H, *m*, $CH_2$), $\delta$ 2.98 (4H, *t*, $J = 8$ Hz, $CH_2 \times 2$), $\delta$ 7.12 (1H, *d*, $J = 10$ Hz, aromatic H), $\delta$ 7.52 (1H, *d*, $J = 10$ Hz, aromatic H), $\delta$ 7.59 (1H, *s*, aromatic H) and $\delta$ 9.82 (1H, *s*, aromatic CHO), suggesting that **1** contained three methylene groups, two aromatic *ortho* coupled protons, one isolated aromatic proton and an aromatic aldehyde.

Finally, the structure of **1** was established as 1H-indene-2,3-dihydro-5-carboxaldehyde by the agreement of IR and PMR with the published spectra [2,3].

Compound **2** also formed a 2,4-dinitrophenylhydrazone, orange needles, mp 259–260°, $C_{10}H_{14}N_4O_4$, $M^+ = 326.1023$. The IR of **2** showed absorption at 1700 $cm^{-1}$ due to the aromatic aldehyde. The PMR in $CCl_4$, showed signals at $\delta$ 2.12 (2H, *m*, $CH_2$), $\delta$ 2.82 (2H, *t*, $J = 8$ Hz, $CH_2$), $\delta$ 3.16 (2H, *t*, $J = 8$ Hz, $CH_2$), $\delta$ 7.31 (3H, *m*, aromatic H) and $\delta$ 10.2 (1H, *s*, aromatic CHO), suggesting that **2** is an isomer of **1**.

**2** therefore must be 1H-indene-2,3-dihydro-4-carboxaldehyde. Although previously synthesized [4], neither of these two aldehydes have been reported before as natural products.

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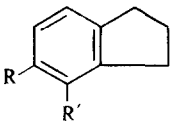


**1**: R = CHO, R′ = H
**2**: R = H, R′ = CHO

REFERENCES

1. Kimura, Y. and Kobayashi, Y. (1957) *Pharm. Bull. Nihon University* **1**, 27
2. Sadtler. *Standard Infrared* **32**, 32 838.
3. Sadtler. *Standard NMR* 4571M.
4. Hunsberger, I. M., Lednicer, D., Gutowsky, H. S., Bunker, D. L. and Taussig, P. (1955) *J. Am. Chem Soc.* **77**, 2466.

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# AEGELINOL, A MINOR LACTONIC CONSTITUENT OF *AEGLE MARMELOS*

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**Key Word Index**—*Aegle marmelos*; Rutaceae; aegelinol; 3′-epimer of decursinol

## INTRODUCTION

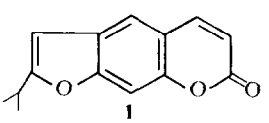
A number of coumarins [1–6], alkaloids [1–3, 6–8], sterols [3, 4, 9] and essential oils [10] have been reported in *Aegle marmelos*. In the course of the present work a new coumarin, aegelinol, has been isolated from the root and stem-bark.

## RESULTS AND DISCUSSION

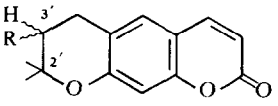
Aegelinol shows the UV absorption of a 2′,2′-dimethylchromeno-3′-hydroxycoumarin ($\lambda_{max}^{EtOH}$ 336 nm; log $\varepsilon$ 4.47; $\lambda_{max}^{EtOH+alkali}$ 320 nm; log $\varepsilon$ 4.55). Strong absorptions at 3400 $cm^{-1}$ (—OH) and 1720 $cm^{-1}$ which indicate a lactone carbonyl, were discernible in the IR spectrum (nujol mull). In its 60 MHz NMR spectrum ($CDCl_3$) characteristic signals were observed for a gem-dimethyl group ($\delta$ 1.42, 6H, *s*), an alcoholic hydroxyl function ($\delta$ 2.51, 1H, *br* signal, disappeared on deuteration), a-C<u>H</u>$_2$-C<u>H</u>-system ($\delta$ 3.04, 1H, *d*, $J = 2.5$ Hz and $\delta$ 2.95, 1H, *d*, $J = 9.0$ Hz; $\delta$ 3.94, 1H, *m*), two aromatic para protons ($\delta$ 6.77 and 7.20, 1H, *s*, each) and the C-3 and C-4 protons of the coumarin nucleus ($\delta$ 6.20 and 7.60, 1H, *d*, each; $J = 9.5$ Hz). The secondary nature of the hydroxyl function (—CH—OH) was apparent from the downfield shift of the methine signal to $\delta$ 5.10 in aegelinol monoacetate, $C_{14}H_{13}O_3$. OCOMe, mp 138°. On dehydration with *p*-toluenesulphonic acid the compound afforded anhydromarmesin (**1**).

From the above data and from the mass fragmentation [*m/e* 264 ($M^+$), 217, 213, 188, 187, 160, 131, 119, 91 and

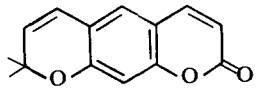
77] a pyranocoumarin structure (**2**) is proposed for aegelinol. This was confirmed by the conversion of aegelinol tosylate (**3**) to xanthyletin (**4**) by refluxing with collidine. The same structure has been reported for decursinol (**5**) [11] but as the optical rotation is of the opposite sign aegelinol must be the 3′-epimer of decursinol (**5**). The absolute configuration at this asymmetric centre (C-3′) in aegelinol was confirmed to be '*R*' by Horeau's methods [12, 13].



**1**



**2** R = α − OH
**3** R = α − OTs
**5** R = β − OH
**6** R = α − OAc



**4**

## EXPERIMENTAL

chromatography and Si gel G (Merck) for TLC.

*Isolation of aegelinol* (**2**). The finely powdered root- and stem-bark of *Aegle marmelos* Correâ (11 kg) were defatted (64 hr) with petrol (bp 60–80°) before extraction (50 hr) with $CHCl_3$ in a Soxhlet. The $CHCl_3$ extract was concd to give marmin, $C_{19}H_{24}O_5$, mp 124–125° and marmesin, $C_{14}H_{14}O_4$, mp 189°. The mother liquor was shaken with 5% citric acid, filtered and the filtrate extracted with $CHCl_3$, washed and dried. The conc $CHCl_3$ extract was chromatographed over Si gel. Colourless crystals (0.0109%) of aegelinol, $C_{14}H_{14}O_4$, ($M^+$ 246), mp 175–177° $[\alpha]_D^{20}$ − 12° ($c$ = 0.83, $CHCl_3$), were obtained by recrystallisation from $C_6H_6$ of the solid obtained in the $C_6H_6$–$CHCl_3$ (2:1) eluates. (Found: C, 68.23; H, 5.65. $C_{14}H_{14}O_4$ requires C, 68.29; H, 5.69%). The monoacetate (**6**) crystallised from petrol –$C_6H_6$, mp 138°. (Found: C, 66.73; H, 5.50. $C_{16}H_{16}O_5$ requires C, 66.66; H, 5.55%). The tosylate (**3**) crystallized from ether, mp 140° (Found: C, 62.88; H, 5.22; S, 7.95. $C_{21}H_{21}O_6S$ requ. C, 62.84; H, 5.24; S, 7.98%).

*Acid catalysed dehydration of* (**2**). Aegelinol (30 mg) was dissolved in dry $C_6H_6$ (25 ml), *p*-toluenesulphonic acid (2 mg) added and the mixture refluxed for 2.5 hr. The product, anhydromarmesin (**1**), crystallised from MeOH, mp 138° (Yield 18 mg). Identity of the sample was confirmed by comparison (co-TLC, mmp and superimposable IR spectra) with an authentic sample. (Found: C, 73.65; H, 5.31. $C_{14}H_{12}O_3$ requires C, 73.67; H, 5.30%).

*Base catalysed dehydration of aegelinol tosylate* (**3**) *with collidine.* Aegelinol tosylate (70 mg) was refluxed with collidine (10 ml) to yield xanthyletin (**4**) (25 mg), mp 128° (crystallised from $C_6H_6$). The compound was identified by comparison (co-TLC, mmp and superimposable IR spectra) with an authentic sample (Found: C, 73.70; H, 5.28. $C_{14}H_{12}O_3$ requires: C, 73.67; H, 5.30%).

*Reaction of aegelinol with racemic α-phenyl butyric anhydride (by Horeau's method).* Racemic α-phenylbutyric anhydride (350 mg) and aegelinol (100 mg) were dissolved in dry Py (5 ml) and left 18 hr. The excess anhydride was decomposed by adding ice-cold $H_2O$ (30 ml) and the aq. soln was extracted twice with EtOAc. The EtOAc extract was washed with 5% aq. $NaHCO_3$ (3 × 10 ml), water and dried. The $NaHCO_3$ washings were washed with $CHCl_3$ to remove any residual neutral matter and subsequently acidified with 3N HCl. The free acid liberated was extracted with $CHCl_3$ and worked up in the usual manner. The free α-phenylbutyric acid was isolated from the $CHCl_3$ soln on evapn. After drying the free acid recorded a rotation $[\alpha]_D^{25} = +0.5°$.

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## REFERENCES

1. Chatterjee, A. and Bhattacharya, A. (1959) *J. Chem. Soc.* 1922.
2. Chatterjee, A. and Mitra, S. S. (1949) *J. Am. Chem. Soc.* **71**, 606.
3. Chatterjee, A. and Chaudhury, B. (1960) *J. Indian Chem. Soc.* **37**, 334.
4. Saha, S. K. and Chatterjee, A. (1957) *J. Indian Chem. Soc.* **34**, 228.
5. Shoeb, A., Kapil, R. S. and Popli, S. P. (1973) *Phytochemistry* **12**, 2071.
6. Basu, D. and Sen, R. (1974) *Phytochemistry* **13**, 2329.
7. Chatterjee, A., Chaudhuri, R. K. and Das, B. C. (1967) *Sci. Cult.* **33**, 279.
8. Chatterjee, A., Bose, S. and Srimany, S. K. (1959) *J. Org. Chem.* **24**, 687.
9. Chatterjee, A. and Roy, S. K. (1959) *J. Indian Chem. Soc.* **36**, 267.
10. Balas, K. K. and Despande, S. S. (1949) *J. Indian Chem. Soc.* **26**, 231.
11. Konoshima, M., Chi, H. J. and Hata, K. (1968) *Chem. Pharm. Bull.* **16**, 1139.
12. Horeau, A. (1961) *Tetrahedron Letters* 506.
13. Horeau, A. and Kagan, H. B. (1964) *Tetrahedron* **20**, 2431.