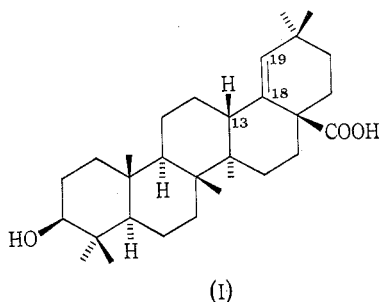


# MOROLIC ACID (3-HYDROXYOLEAN-18-EN-28-OIC ACID) FROM THE BARK OF *EUCALYPTUS PAPUANA* F. MUELL.\*

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*Eucalyptus papuana* F. Muell. (syn. *E. papuana* var. *aparrerinja* Blakely), which grows commonly in central Australia and sparsely in northern Australia and Papua, is known as the "ghost gum" because of the intense whiteness of its trunk, branches, and twigs. This whiteness is due to a powder which comes off when rubbed and is used by the aborigines as a pigment.<sup>1</sup> Bark scraped from the surface of the trunk yields about 20% by weight of crystalline triterpenes, and it appears to be this material which is responsible for the unusual appearance of the tree. The triterpenes consist largely of morolic acid<sup>2</sup> (3-hydroxyolean-18-en-28-oic acid, I) which has previously been isolated only from a saponin found in the heartwood of *Mora excelsa* Benth.<sup>3</sup> and from *Agauria salicifolia* Hook.<sup>4,5</sup>



When the crude triterpenes from *E. papuana* bark are esterified with diazomethane and the esters chromatographed on alumina as much as 70% of the total is recovered as methyl morolate. The bark is therefore a very convenient source of morolic acid. In chromatographing the methyl esters no methyl morolate acetate was detected in the early fractions from the column, showing that morolic acid acetate is not present in the original triterpene acids.

According to Blakely's classification<sup>1</sup> *E. papuana* belongs to the series *Corymbosae*, and like other members of this group its leaf wax does not contain long-chain  $\beta$ -diketones of the type found in the leaf waxes of many *Eucalyptus* species.<sup>6</sup> It was previously noted<sup>6</sup> that the fruits of *E. polycarpa* (*Corymbosae peltatae*) are coated with triterpenes; these have not been fully examined but they do not contain any appreciable quantity of morolic acid, and the major component is probably ursolic acid. The isolation of morolic acid from *E. papuana* and of 11,12-dehydroursolic lactone acetate from several *Eucalyptus* species<sup>7</sup> suggests considerable variation in the triterpenes occurring in this genus.

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<sup>1</sup> Blakely, W. F., "A Key to the Eucalypts." 2nd Ed. (Forestry and Timber Bureau: Canberra 1955.)

<sup>2</sup> Barton, D. H. R., and Brooks, C. J. W., *J. Chem. Soc.* 1951, 257.

<sup>3</sup> Barton, D. H. R., and Brooks, C. J. W., *J. Amer. Chem. Soc.*, 1950, **72**, 3314.

<sup>4</sup> Sosa, A. and Dussy, J., *C. r. hebdomadaire Séances Acad. Fr.*, 1951, **232**, 2249.

<sup>5</sup> Dussy, J. and Sosa, A., *Bull. Soc. Chim. Biol.*, 1951, **33**, 1672, 1697.

<sup>6</sup> Horn, D. H. S., Kranz, Z. H., and Lamberton, J. A., *Aust. J. Chem.*, 1964, **17**, 464.

<sup>7</sup> Horn, D. H. S., and Lamberton, J. A., *Aust. J. Chem.*, 1964, **17**, 477.

### Experimental

Surface bark scrapings of *E. papuana* were obtained from several trees growing near Alice Springs in central Australia. A sample (12.6 g) yielded on continuous extraction with chloroform crude crystalline triterpene acids (2.5 g). The methyl esters prepared by reaction with diazomethane were chromatographed on Woelm neutral alumina of activity I, to which 1% water had been added. The major fractions eluted by benzene and benzene/ether mixtures were crystalline, and consisted of methyl morolate (70% yield). The fractions eluted later were gummy, and although their infrared spectra suggested the presence of more methyl morolate they could not be crystallized. After crystallization from an ethyl acetate/methanol mixture methyl morolate had m.p. 228–229°,  $[\alpha]_D^{18} +29.2^\circ$  (c, 1.38) (Barton and Brooks<sup>4</sup> reported m.p. 228–229°,  $[\alpha]_D +26^\circ$ ) and was identified by mixed melting point determination and by comparison of its infrared absorption spectrum with that of an authentic specimen of methyl morolate (Found: C, 78.8; H, 10.5. Calc. for  $C_{31}H_{50}O_3$ : C, 79.1; H, 10.7%). It yielded an acetate, m.p. 263–264°,  $[\alpha]_D^{18} +39.2^\circ$  (c, 1.74) [Barton and Brooks<sup>5</sup> reported m.p. 263–264°,  $[\alpha]_D +37^\circ$  (c, 1.82) and  $[\alpha]_D +38^\circ$  (c, 1.76)] which was identified by a similar comparison with authentic methyl morolate acetate. The acetate was further characterized by its n.m.r. spectrum, which showed a one-proton peak at  $\delta$  5.09 (in  $CDCl_3$  solution, and relative to tetramethylsilane  $\delta$  0.00) assigned to the olefinic proton at C 19. The signal showed fine splitting presumably due to long-range coupling with the allylic proton at C 13.

Wax from the leaves of *E. papuana* had an infrared spectrum indicating the presence of esters, free alcohols, and acids (probably triterpenoid), but  $\beta$ -diketones<sup>6</sup> were absent.

Crude triterpenes from the fruits of *E. polycarpa* were acetylated (acetic anhydride/pyridine) and methylated (diazomethane). Chromatography on alumina gave crystalline fractions having infrared spectra almost identical with that of methyl ursolate acetate, but they were evidently mixtures as their melting points were indefinite and somewhat lower than the melting point of methyl ursolate acetate.

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