

NIMBININ : A NEW TETRANORTRITERPENOID<sup>†</sup>  
C.R. Narayanan, R.V. Pachapurkar and (in part)  
B. M. Sawant  
National Chemical Laboratory, Poona, India

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THE  $\alpha\beta$ -epoxy- $\delta$ -lactone present in the tetranortriterpenoids related to limonin (1), is presumed to originate from a precursor having an  $\alpha\beta$ -epoxy-16-ketone in the D-ring by a Baeyer-Villiger type of oxidation. One of this type has very recently been reported (2). We wish now to report another such precursor from a different source and with an advanced state of oxidation in ring A.

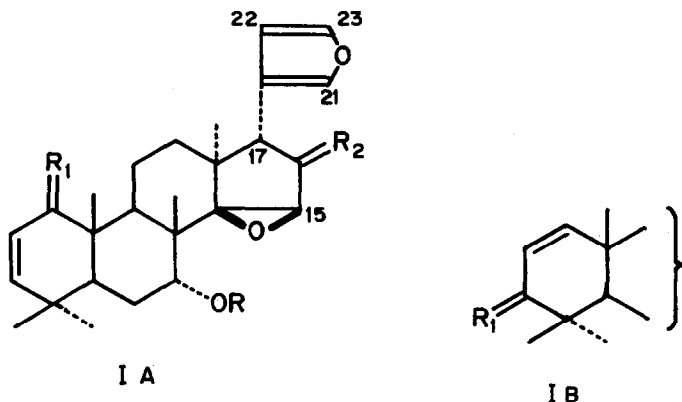
In continuation of our work on nimbin (3,4,5,6,7), its mother liquors were exhaustively chromatographed to give several minor products. One of this readily crystallised, nimbinin<sup>\*</sup> IA or IB, C<sub>28</sub>H<sub>34</sub>O<sub>6</sub> (M<sup>+</sup> 466), m.p. 202-204<sup>o</sup>,  $[\alpha]_D^{25} +45^o$  (CHCl<sub>3</sub>),  $\lambda_{\max}^{\text{EtOH}}$  219 m $\mu$ ,  $\epsilon = 18000$ ,  $\mu_{\max} 1750$  ( $\alpha\beta$ -epoxy cyclopentanone), 1730 (acetate), 1670 (cyclohexenone) and 1500 and 878 cm<sup>-1</sup> ( $\beta$ -substituted furan). Its NMR spectrum showed peaks at  $\delta$  7.58 (21-H), 7.33 (23-H), 6.22 (22-H), typical AB quartet with doublets centred at  $\delta$  7.1 and 5.8 (J = 10 cps) (ring A vinyl protons), triplet centred at  $\delta$  4.66 (J = 2.5 cps) (7 $\beta$ -H), singlet at 3.82 (17-H), sharp singlet at  $\delta$  3.3 (15-H), acetate methyl at  $\delta$  2.01 and five tertiary methyl groups at  $\delta$  1.17, 1.15, 1.00 (2) and 0.98. These spectral properties had marked

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<sup>\*</sup>First isolated from the mother liquors of nimbin by S. Siddiqui and C.R. Mitra, Curr. Sci. (India), 11, 274 (1942); J. sci.industr.Res. (India) 4, 5 (1945); 8B 188 (1949) and called nimbinin.

resemblance to those of grandifoliene (2) in the B,C,D rings.



I (A or B)	R = Ac, R <sub>1</sub> =R <sub>2</sub> =O
II "	R = Ac, R <sub>1</sub> =R <sub>2</sub> =N-OH
III "	R = Ac, R <sub>1</sub> =R <sub>2</sub> =O, ring A double bond saturated.
IV "	R = H, R <sub>1</sub> =R <sub>2</sub> =O

Nimbinin readily formed a dioxime, C<sub>28</sub>H<sub>36</sub>O<sub>2</sub>N<sub>2</sub>, II (A or B), m.p. 172-75°, [α]<sub>D</sub> +68° (CHCl<sub>3</sub>), whose IR showed the absence of absorptions at 1750 and 1670 cm<sup>-1</sup>, thus confirming the presence of the two keto groups. Hydrogenation of I on Pd/c with one mole of hydrogen gave dihydronimbinin III (A or B), C<sub>28</sub>H<sub>36</sub>O<sub>2</sub>, m.p. 195°, [α]<sub>D</sub> +8° (CHCl<sub>3</sub>), in whose IR the 1670 cm<sup>-1</sup> band of I had moved up to 1708 cm<sup>-1</sup> consistent with the hydrogenation of the double bond in ring A. Its NMR spectrum showed, besides the disappearance of the AB quartet of I, the upfield shift of one of the methyl groups by 0.09 PPM, as in nimbin to dihydronimbin (3-6). Subtraction curve of dihydronimbinin from nimbinin gave a curve λ<sub>max</sub> 228 mμ ε = 11000, (nimbin - dihydronimbin λ<sub>max</sub> 229 mμ ε = 7600).

Spin decoupling of 17-H in I, sharpened the signal of the 21-H, in complete agreement with its allylic location and pseudo-axial disposition. Hydrolysis of I gave desacetylnimbinin (IV), C<sub>26</sub>H<sub>32</sub>O<sub>7</sub>, m.p. 193-95°, [α]<sub>D</sub> +64° (CHCl<sub>3</sub>), ν<sub>max</sub> 3400 cm<sup>-1</sup> (C<sub>7</sub> α-OH), 1660 cm<sup>-1</sup> and 1750 cm<sup>-1</sup> (the two ketones). The downfield shift of the C<sub>15</sub>-H in it to δ 3.51 (from 3.3 in I), and the large positive shift of the rotation, is characteristic of the

hydrolysis of the C<sub>7</sub>-acetate in such systems as in the B,C,D rings (2,8).

Work is in progress to distinguish between structures IA and IB for nimbinin (9).

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- 9 Since this manuscript was prepared for publication, the issue No.6 (p.278, 1967) of Chem. Comm. received in our library contained an article by D. Lavie and M.K.Jain on epoxyazadiradione. Though this compound and its dihydroderivative have similar m.ps as ours (many of these compounds have m.ps around 200°C, e.g. nimbin, dihydronimbin, gedunin, andirebin, nimbinin, dihydronimbinin etc. and mixed m.ps. e.g. nimbin + dihydronimbin, nimbinin + dihydronimbinin, often do not show any depression) the rotations of their compounds and the direction of change of rotation on hydrogenation are very different from those of ours, and hence it is not possible at this stage to decide whether the two compounds are the same or different.