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#### SOME NEW HYDROXY SANDARACOPIMAR-15-ENES FROM *PREMNA LATIFOLIA* ROXB.

WE report in this communication the isolation and constitution of four diterpene alcohols from the root-bark of *Premna latifolia* Roxb. (Verbenaceae). The residues obtained from *n*-hexane extracts were chromatographed over silica gel, after removal of latex, when the four compounds A, B, C and D separated out and their properties are recorded below. All these compounds gave red Liebermann-Burchard test.

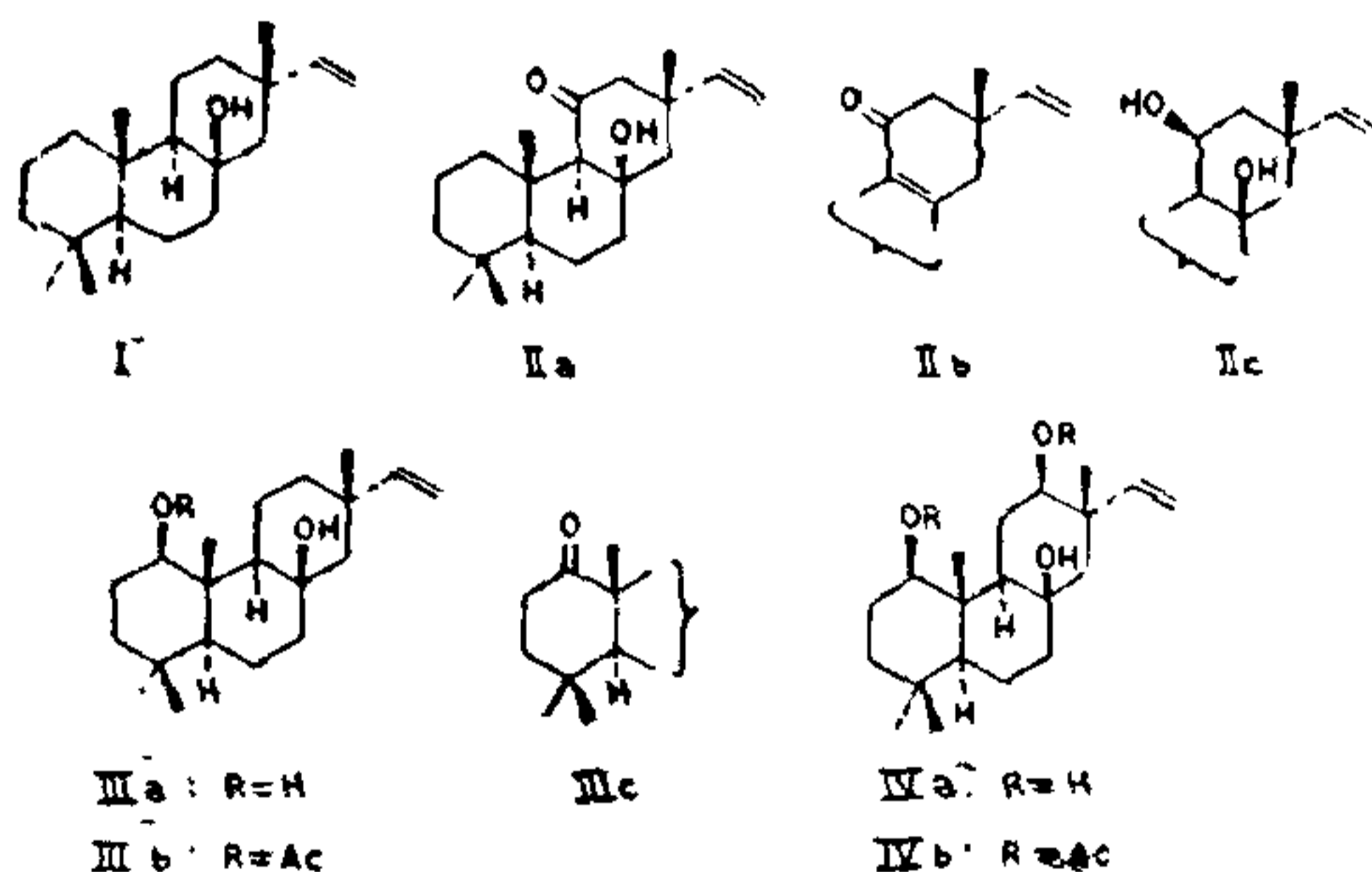
Compound-A appeared as colourless needles from *n*-hexane, m.p. 42–43° (C<sub>20</sub>H<sub>34</sub>O; m/e M<sup>+</sup>, 290), [α]<sub>D</sub><sup>20</sup> – 6.6° (c, 1.0, CHCl<sub>3</sub>); no absorption in the U.V. above 200 nm; I.R.  $\nu_{\text{max}}^{\text{CCl}_4}$  cm<sup>-1</sup> 3620 (–OH), 3090, 1820, 1640 and 910 (vinyl), 1390, 1370 (gem dimethyl) and <sup>1</sup>H NMR (XL-100 spectrum) CCl<sub>4</sub> (δ) 0.85 (s, 6H, two *t*-CH<sub>3</sub>), 0.97 (s, 3H, *t*-CH<sub>3</sub>), 1.19 (s, 3H, *t*-CH<sub>3</sub>) and an ABX pattern characteristic of vinyl group (4.73, dd, J = 10.5, 1.5 Hz, 1H; 4.77,

dd, J = 17.5, 1.5 Hz, 1H and 5.63, dd, J = 17.5, 10.5 Hz, 1H). The presence of five terminal pendant groups, viz., four *t*-methyls and a vinyl group, besides its molecular formula suggest a pimarane, rosane or cassane type structure for compound-A. A survey of literature reveals that these characteristics are in agreement with those recorded for sandaracopimar-15-en-8β-ol (I) which was isolated by Corbett *et al.*<sup>1</sup> from *Dacrydium colensoi* and Bohlmann *et al.*<sup>2,3</sup> from *Garuleum pinnatifidum* DC., *G. bipinnatum* Less., *Osteospermum fruticosum* (L.) Norl., *O. junceum* Berg., *O. corymbosum* and *O. rotundifolium*.

Compound-B crystallised from *n*-hexane as colourless needles, m.p. 204–206° (C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>; m/e M<sup>+</sup>, 304), [α]<sub>D</sub><sup>20</sup> – 5.5° (c, 1.0, pyridine); no absorption in the U.V. above 200 nm; I.R.  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup> 3370 (–OH), 3080, 1820, 1635 and 915 (vinyl), 1698 (six membered ketone) and 1375, 1395 (gem dimethyl) and <sup>1</sup>H NMR (XL-100 spectrum) CCl<sub>4</sub> (δ) 0.85 (s, 6H, two *t*-CH<sub>3</sub>), 1.22 (s, 3H, *t*-CH<sub>3</sub>), 1.24 (s, 3H, *t*-CH<sub>3</sub>), an ABX pattern of vinyl (4.86, dd, J = 10.5, 1.5 Hz; 1H; 4.90, dd, J = 17.5, 1.5 Hz, 1H and 5.76, dd, J = 17.5, 10.5 Hz, 1H) and 2.08–2.47 (broad, 4H). It did not form a 2, 4-dinitrophenylhydrazone, perhaps, the carbonyl is hindered. Further, it did not yield an acetate with Ac<sub>2</sub>O/pyridine indicating that the hydroxyl is either hindered or tertiary. The presence of five terminal pendant groups, the molecular formula, besides the co-occurrence of I indicates that it could well be considered as sandaracopimar 15-en-8β-ol with a carbonyl function. The position of the carbonyl group could be established by dehydration using *p*-toluenesulphonic acid, when a liquid (C<sub>20</sub>H<sub>30</sub>O) was obtained, U.V.  $\lambda_{\text{max}}^{\text{EtOH}}$  252 nm (log ε, 3.92) indicating α, β-unsaturated ketone further confirmed by I.R.  $\nu_{\text{max}}^{\text{liq. film}}$  1665 cm<sup>-1</sup> and absence of hydroxyl bands. It formed a 2, 4-dinitrophenylhydrazone, m.p. 155–157° (C<sub>20</sub>H<sub>34</sub>O<sub>4</sub>N<sub>4</sub>). The <sup>1</sup>H NMR spectrum in CCl<sub>4</sub> showed no mere olefinic protons besides the three vinylic hydrogens, thereby showing that the double bond formed was tetra-substituted and reasonably assumed to be Δ<sup>8,9</sup>. The carbonyl function could then be present in 7, 11 or 14 positions, and out of these 11 position was preferred in order to account for a single proton signal at 2.73 (δ), dm, J = 13 Hz assignable<sup>17,2</sup> to C1-β H in this anhydro ketone, the constitution of which could be represented as sandaracopimar-8, 15 dien-11-one (II b) and the starting keto alcohol is 8β hydroxysandaracopimar 15-en-11-one (II a). Sodium borohydride reduction of II a gave a diol (II c), m.p. 158–162 (C<sub>20</sub>H<sub>34</sub>O<sub>2</sub>), [α]<sub>D</sub><sup>20</sup> + 21.6° (c, 1.0, CHCl<sub>3</sub>) which neither reacted periodic acid nor could be acetylated with Ac<sub>2</sub>O/pyridine and showed in <sup>1</sup>H NMR spectrum a single proton signal at 4.44 δ, broad w<sub>1</sub> 7 Hz assignable

to methine proton of  $-\text{CHOH}$  group, indicating that this hydrogen is equatorial and the hydroxyl  $\beta$ -axial. This diol is considered to be a C11-epimer of sandaracopimar-15-en-8 $\beta$ , 11 $\alpha$ -diol, described by Bohlmann *et al.*<sup>2</sup>

The compound-C crystallised as colourless needles from *n*-hexane, m.p. 160 (C<sub>20</sub>H<sub>34</sub>O<sub>2</sub>, m/e M<sup>+</sup>, 306);  $[\alpha]_D^{30} - 15.2^\circ$  (c, 2.5, CHCl<sub>3</sub>); U.V. no absorption above 200 nm; I.R.  $\nu_{\text{max}}^{\text{CCl}_4} \text{ cm}^{-1}$  3635 and 3480-3520 (hydroxyls), 3100, 1825, 1640 and 915 (vinyl) 1395, 1375 (gem dimethyl); <sup>1</sup>H NMR (XL-100 spectrum) CCl<sub>4</sub>,  $\delta$ , 0.85 (s, 6H, two *t*-CH<sub>3</sub>), 0.99 (s, 3H, *t*-CH<sub>3</sub>), 1.17 (s, 3H, *t*-CH<sub>3</sub>), 2.34 (ddm, J = 14, 4 Hz, 1H), 3.24 (dd, J = 9.6 Hz, 1H) and an ABX pattern of vinyl (4.72, dd, J = 10.5, 1.5 Hz, 1H; 4.77, dd, J = 17.5, 1.5 Hz, 1H and 5.63, dd, J = 17.5, 10.5 Hz, 1H). These data clearly suggest that compound-C also possesses sandaracopimar-15-en-8 $\beta$ -ol moiety. Hydrogenation over palladium catalyst gave a dihydro derivative, m.p. 154.5° (C<sub>20</sub>H<sub>36</sub>O<sub>2</sub>). The second oxygen is present in sec. alcohol as a monoacetate, m.p. 108-111° (C<sub>22</sub>H<sub>36</sub>O<sub>2</sub>, III b) and a ketone, m.p. 207-208° (C<sub>22</sub>H<sub>32</sub>O<sub>2</sub>, III c) could be prepared.



The methine proton of  $-\text{CHOH}$  in compound-C, which appeared at 3.24  $\delta$  was deshielded to 4.49  $\delta$ , t, J = 7 Hz in its acetate and the  $w_2$  of 15 Hz of this signal in either case indicate that it is axially oriented. The compound neither cleaved with periodic acid nor formed an acetonide and further dehydration of its ketone did not yield an  $\alpha$ ,  $\beta$ -unsaturated product. The splitting pattern of the methine signal, under these circumstances, suggests 1, 3 or 12 positions for the sec. hydroxyl. Sandaracopimar-15-en-8 $\beta$ , 12 $\beta$ -diol, which was described earlier by Bohlmann *et al.*<sup>2</sup> differs from compound-C. Secondary hydroxyl in 1-position was preferred in order to account for a single proton signal at 2.34  $\delta$  which could well be assigned to 11 $\alpha$ -hydrogen. The paramagnetic effect of 11 $\alpha$ -OH on 1 $\beta$ -H in this series of compounds has been amply justified by Bohlmann and coworkers<sup>2,3,4</sup>

Now in the present case, 1 $\beta$ -OH exerts a similar effect on 11 $\alpha$  equatorial proton. Further, sandaracopimar-15-en-8 $\beta$ , 11 $\beta$ -diol (II c) has been described above and its 11 $\alpha$  epimer was reported earlier<sup>2</sup> and these two compounds differ very much from compound-C which may now be represented as sandaracopimar-15-en-1 $\beta$ , 8 $\beta$ -diol (III a).

The compound-D was obtained as colourless needles from benzene, m.p. 198.5-200° (C<sub>20</sub>H<sub>34</sub>O<sub>3</sub>, m/e M<sup>+</sup>, 322);  $[\alpha]_D^{30} - 33.6^\circ$  (c, 1.0, CHCl<sub>3</sub>); U.V. no absorption above 200 nm; I.R.  $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$ , 3480-3310 (hydroxyls), 3090, 1620, 910 (vinyl) and 1390, 1380 (gem dimethyl); <sup>1</sup>H NMR (XL-100 spectrum) CDCl<sub>3</sub>,  $\delta$ , 0.84 (s, 6H, 2  $\times$  *t*-CH<sub>3</sub>), 1.04 (s, 3H, *t*-CH<sub>3</sub>), 1.20 (s, 3H, *t*-CH<sub>3</sub>), 2.34 (m, 1H), 3.39 (t, J = 7 Hz, 1H), 3.42 (t, J = 7 Hz, 1H) and an ABX pattern characteristic of vinyl (4.81, dd, J = 10, 1.5 Hz, 1H; 4.85, dd, J = 17.5, 1.5 Hz, 1H and 5.74, dd, J = 17.5, 10 Hz, 1H). On hydrogenation over Adams catalyst it gave the dihydrotriol, m.p. 208° (C<sub>20</sub>H<sub>36</sub>O<sub>3</sub>); and on acetylation a diacetate (IV b), m.p. 165-166° (C<sub>24</sub>H<sub>38</sub>O<sub>5</sub>) in which the methine protons of  $-\text{CHOAc}$  appeared as triplets at 4.55 and 4.56  $\delta$ , J = 7 Hz indicating an axial configuration, besides these signals could be taken as X parts of ABX patterns. It could reasonably be assumed, in the light of the facts presented, that compound-D also belongs to sandaracopimar-15-en-8 $\beta$ -ol series with two additional hydroxyls. From a study of the spectral characteristics of the derivatives and also a keto-diol, m.p. 180-182° (C<sub>20</sub>H<sub>32</sub>O<sub>3</sub>) obtained as a minor product in oxidation using pyridine-chromium trioxide, the two secondary hydroxyls could be tentatively placed at 1 and 12 positions (IV a); further investigation is in progress to establish this.

Fuller details will be published elsewhere.

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