

STEREOCHEMISTRY OF TREVOAGENIN A AND B AND  
CONFIGURATION AT C<sub>24</sub> OF THE 2OR-OCOTILLONES

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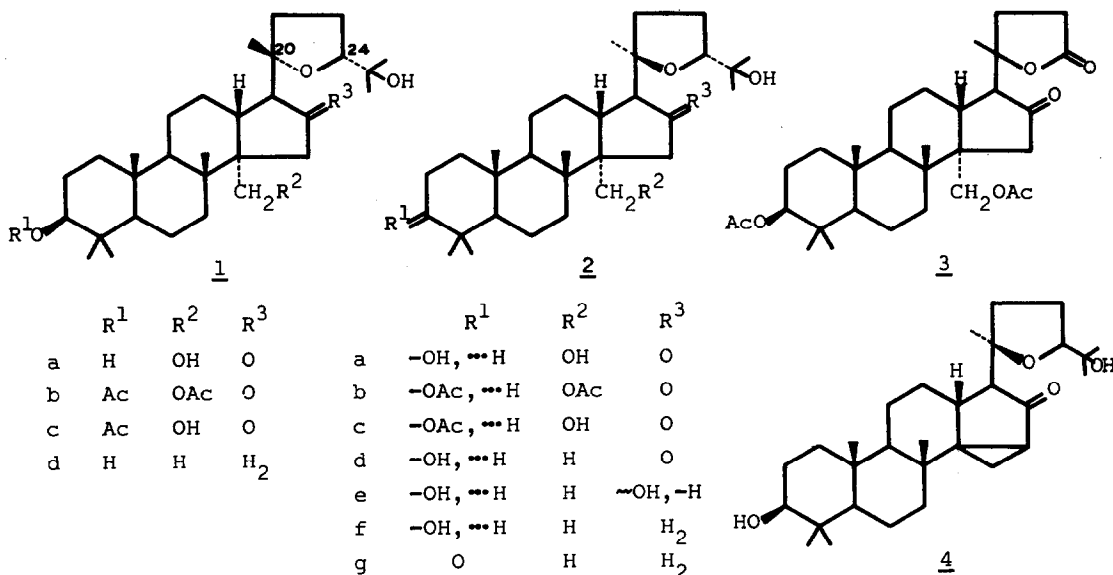
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Of the triterpenes of the ocotillol type till now only the stereochemistry of the isomers of the 2OS-series has been established.<sup>1</sup> Our work reports the configuration at C<sub>24</sub> of the isomers of the 2OR-series<sup>2-4</sup> as a consequence of the determination of the stereochemistry of trevoagenin A (2a) and B (1a), recently isolated from Trevoa trinervis Miers.<sup>5</sup> In acid medium (2N HCl in EtOH at reflux for 2 h)<sup>6</sup> both trevoagenins equilibrate at C<sub>20</sub>, via a carbonium ion stabilized by the presence of a keto group at C<sub>16</sub>, to yield an equimolar mixture of (1a) and (2a). Therefore, both compounds must have the same stereochemistry at C<sub>24</sub> and differ in that at C<sub>20</sub>. This is also in agreement with the finding that Jones oxidation of the corresponding diacetates (1b) and (2b) gives different lactones (3) (2OS or 2OR).<sup>5</sup>

In order to determine the configuration at C<sub>20</sub> and C<sub>24</sub> trevoagenin B diacetate (1b) was selectively saponified with methanolic Na<sub>2</sub>CO<sub>3</sub> to give the monoacetate (1c), m.p. 214-216°, [ $\alpha$ ]<sub>D</sub> -10°, which was oxidized with Collins reagent. Huang-Minlon reduction of the resulting ketoaldehyde gave ocotillol-II (1d), m.p. 196-198°, [ $\alpha$ ]<sub>D</sub> +28°, identical with an authentic sample (m.m.p., tlc, ir, nmr). This chemical correlation led to establish unequivocally the configuration 2OS,24R for trevoagenin B (1a) and hence 2OR,24R for trevoagenin A (2a).

On the other hand, the configuration at C<sub>24</sub> of the 2OR-ocotillones was determined as follows. Trevoagenin A monoacetate (2c), m.p. 249-251°, [ $\alpha$ ]<sub>D</sub> -25°, obtained as described above, was treated with TsCl in pyridine and the tosylate solvolyzed with NaOAc in aqueous acetone at reflux to give the acetate of (4), m.p. 243-246°, [ $\alpha$ ]<sub>D</sub> +62°, which on saponification yielded (4), m.p. 267-269°, [ $\alpha$ ]<sub>D</sub> +37°, M<sup>+</sup> 472,  $\nu_{\text{max}}^{\text{KBr}}$  3050, 3020, 1700 cm<sup>-1</sup>,  $\lambda_{\text{max}}^{\text{EtOH}}$  201 nm ( $\epsilon$  5600). Reduction



of (4) with Li in liquid NH<sub>3</sub> gave a mixture of (2d) {m.p. 238-240°, [ $\alpha$ ]<sub>D</sub> -45°, M<sup>+</sup> 474,  $\nu_{\text{max}}^{\text{KBr}}$  1725 cm<sup>-1</sup>} and (2e) {m.p. 216-218°, [ $\alpha$ ]<sub>D</sub> +30°}. Huang-Minlon elimination of the keto group in (2d) afforded (2f), m.p. 155-158°, [ $\alpha$ ]<sub>D</sub> +14°, which was oxidized with Collins reagent to (2g). This compound was shown to be identical (m.m.p., tlc, ir, nmr) with 20R,24 $\xi$ -ocotillone<sup>4</sup> whose configuration at C<sub>24</sub> therefore must be R. Moreover, we may deduce that 20 $\xi$ <sub>1</sub>-ocotillone<sup>2</sup> and kapurol<sup>3,7</sup> must have the configuration 20R,24 $\xi$  since both compounds can be degraded to the same trisnor-lactone as 20R,24 $\xi$ -ocotillone.<sup>4</sup>

All new compounds gave correct elemental analyses. Optical activities were determined in CHCl<sub>3</sub>. We thank Prof. G. Ourisson, Dr. R.E. Wolff (Université Strasbourg) and Dr. I. Wahlberg (Swedish Tobacco Co., Stockholm) for samples.

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- 6) On increasing the reflux time other products are obtained; see A.G. González, M. Cortés & E. Suárez, Chem. Commun., in press.
- 7) Kapurolone and 20 $\xi$ <sub>1</sub>-ocotillone have the same physical constants, which suggests that they are identical.