Tetrahedron Vol 40, No 2, pp 419 to 420, 1984
Printed in Great Britain

0040-4020/84 $3.00 + .00
Pergamon Press Ltd.

THE X-RAY STRUCTURE OF METHYL SHOREATE AND THE STEREOCHEMISTRY OF EICHLERIANIC ACID, CABRALEONE AND OCOTILLONE

DAVID LAVIE,* FELIX FROLOW and HAIM MESHULAM
Departments of Organic and Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel

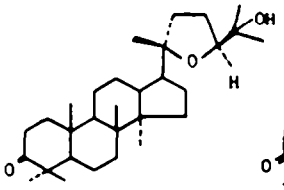
(*Received in the UK 4 January* 1983)

Abstract—An X-ray structure determination of methyl shoreate has shown that this compound has 20S,24R stereochemistry in the side chain. Ocotillone therefore possesses the same configuration, whereas eichlerianic acid and cabraleone must have 20S,24S stereochemistry. A previous wrong assignment is thereby corrected.

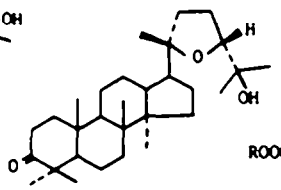
In a paper published in this journal a number of years ago,[1] the isolation and identification of a number of dammarane triterpenes from a brasilian tree *Cabralea eichleriana* D.C. (Meliaceae) was reported and discussed. Among the compounds isolated and interrelated were two C-24 epimeric ketones identified as cabraleone (**1**) and ocotillone (**2**) and two acids, one shoreic acid (**3a**), previously isolated from different species of *Shorea*,[2,3] and the second eichlerianic acid (**4**), reported then for the first time.[1] The latter was found to be an epimer of shoreic acid at C-24. The identity of shoreic acid (**3a**) was unequivocally confirmed by comparison of its methyl ester **3b** with an authentic sample, kindly supplied by Prof. R. E. Wolff, who informed us at the time that the structure of methyl shoreate had been determined by X-ray analysis and was given as unpublished information (see note added in proof in Ref. 3); it referred to a 20S,24S configuration for the side chain. Based on this information, we assigned a 20S,24R configuration for eichlerianic acid.

Since cabraleone (**1**) and eichlerianic acid (**4**) were interrelated by photolysis of the former to dihydromethyl eichlerianate,[1] we suggested that cabraleone also possess the same 20S,24R configuration, and therefore a 20S,24S configuration was assigned to its epimer ocotillone (**2**). These assignments were in contradiction with the configurations 20S,24S given to cabraleone,[4] and 20S,24R to ocotillone,[5] which were based on the X-ray structure of the bromocompound **5** obtained by the treatment of betulafolienetriol (**6**) with NBS, and a sequence of reactions which related compounds, **6**, **5** and 3-acetyl dammarenediol, with ocotillone and cabraleone.[5] To account for the discrepancies in the configurational allocations, and since it was believed that the X-ray structure of shoreic acid as reported was correct,[3] it was then suggested that an inversion of configuration at C-24 had taken place during the interrelation of compound **5** with ocotillone.[1] However, later Tanaka *et al.*[6] checked the chemical correlation in view of new developments, and concluded that the configuration at C-24 of ocotillone (**2**) and its related triterpenes should be 24R.

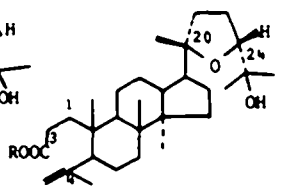
In view of these renewed observations, together with the fact that no paper on the X-ray structural



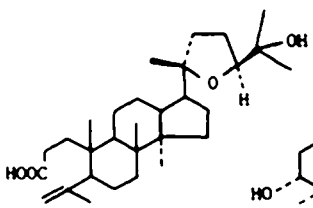
1



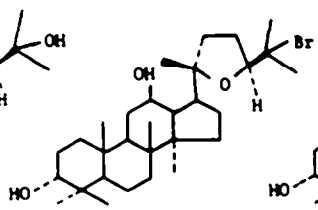
2



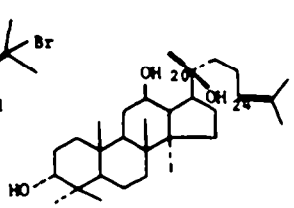
3a, R=H
3b, R=Me



4



5



6

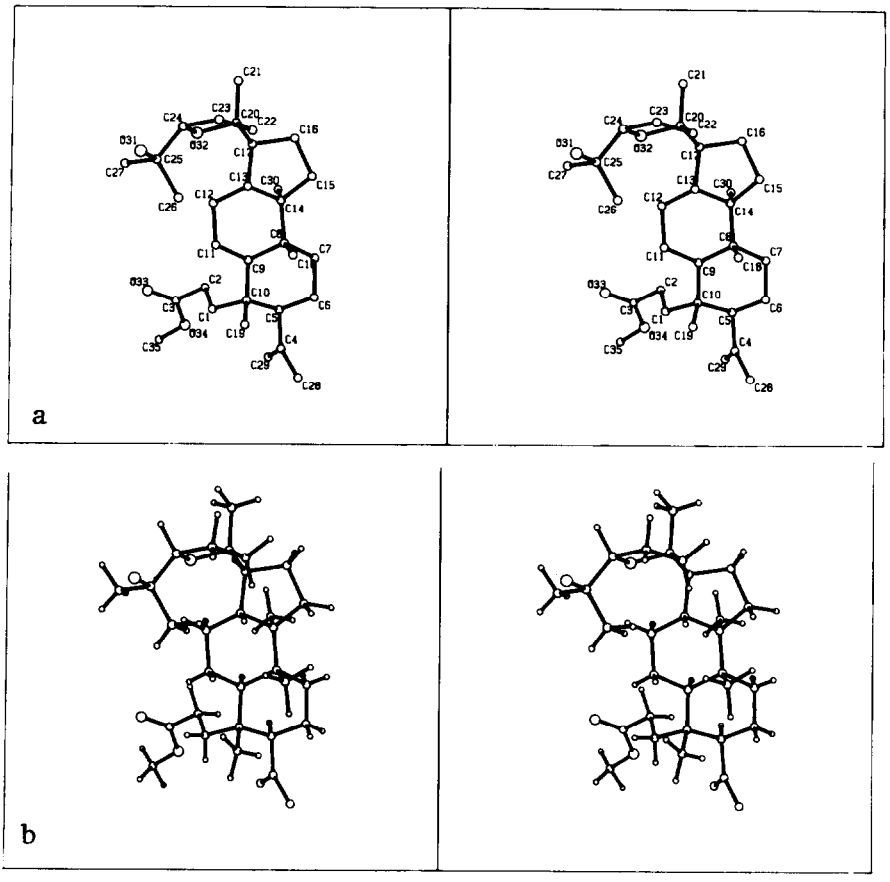


Fig. 1. Stereoscopic view of methyl shoreate: (a) with numbering; (b) with hydrogens.

analysis of methyl shoreate has been published so far, it was felt necessary to determine unequivocally the configuration of shoreic acid. To this end an X-ray analysis of methyl shoreate (**3b**) was carried out. From the stereoscopic view shown in Fig. 1, it can be seen that the configuration at the side chain is 20S,24R. Ocotillone (**2**) has therefore the same configuration, and hence eichlerianic acid (**4**) and cabraleone (**2**) possess a 20S,24S configuration at their side chains.

EXPERIMENTAL

X-ray single-crystal analysis was made using three-dimensional intensity data, collected on a computer controlled Enraf-Nonius CAD-4 diffractometer [λ(Mo–K$\bar{\alpha}$) = 0.7114 Å] by ω-2θ technique ($\theta \leqslant 27°$) at room temperature. *Crystal data*: orthorhombic, $a = 7.818(1)$, $b = 12.458(2)$, $c = 29.366(3)$ Å, space group $P2_12_12_1$, and $Z = 4$. The structure was solved by direct methods using 2531 unique reflections with $F_O > 3\sigma(F_O)$. The nonhydrogen atoms were refined with anisotropic temperature factors. All hydrogens except these of the terminal CH_2 and the adjacent CH_3 groups (atoms C-28 and C-29), were found from a difference Fourier map and refined without constraints (C–H bonds ranged between 1.20 and 0.82 Å) with overall isotropic temperature factor ($U = 0.08$ Å^2). The failure to find the five hydrogens mentioned above is probably due to statistical disorder on this site of the molecule. Block diagonal least-squares refinement converged to $R = 0.07$. The final difference Fourier map revealed only randomly distributed electron density (maximum peak of 0.3 eÅ^{-3}). Data have been deposited at the Cambridge Crystallographic Data Center.

REFERENCES

[1]M. M. Rao, H. Meshulam, R. Zelnik and D. Lavie, *Phytochemistry* **31**, 333 (1975).
[2]J. P. Lantz and R. E. Wolff, *Bull. Soc. Chim. France* 2131 (1968).
[3]N. G. Bisset, V. Chavanel, J. P. Lantz and R. E. Wolff, *Phytochemistry* **10**, 2451 (1971); see note added in proof.
[4]S. C. Cascon and K. S. Brown, *Tetrahedron* **28**, 315 (1972).
[5]M. Nagai, N. Tanaka, S. Ichikawa and O. Tanaka, *Tetrahedron Letters* 4239 (1968).
[6]O. Tanaka and S. Yahara, *Phytochemistry* **17**, 1353 (1978).