

Chemical studies of marine invertebrates. VIII.<sup>(1)</sup>  
Africanol, an unusual sesquiterpene from *Lemmalia africana*  
(Coelenterata, Octocorallia, Alcyonacea).

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Whilst the occurrence of terpenoids in Gorgonians is well documented<sup>(2)</sup>, the presence of such compounds in the closely related Alcyonarians has not yet been reported. During a systematical chemical screening of these marine invertebrates, we have found many species to be a rich source of sesqui- and diterpenes. We wish to report the structure of africanol, a sesquiterpene isolated from *Lemmalia africana* (May, 1898).

Specimens of *L. africana* were collected around the island of Leti, province of Maluku, Indonesia<sup>(3)</sup>. Sun-dried animals were extracted with methylene chloride and the resulting extract submitted to repetitive silicagel column chromatography. This procedure afforded, with a yield of 0.3 % (dry weight), a crystalline compound : africanol (I) (C<sub>15</sub>H<sub>26</sub>O ; molecular ion at m/e 222 ; m.p. : 58-60° ; (α)<sub>CHCl<sub>3</sub></sub><sup>579</sup> : + 59.5° (c = 0.474) ; UV (CH<sub>3</sub>OH) : end absorption).

The IR spectrum indicated the presence of an hydroxyl group (ν<sub>OH</sub> at 3500 cm<sup>-1</sup>) which had to be tertiary since it could not be acetylated under usual conditions.

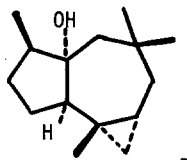
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<sup>o</sup> Chargé de Recherches du F.N.R.S.

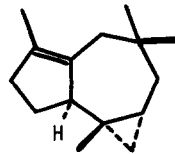
Moreover, the  $^1\text{H}$  NMR spectrum <sup>(4)</sup> of africanol is devoid of any signal below 2.2 ppm. It shows three tertiary methyl groups, appearing as 3H singlets at 0.95, 1.00 and 1.10 ppm, and one secondary methyl group (doublet at 0.88 ppm;  $J = 7$  Hz). A two protons absorption between 0.1 and 0.75 ppm suggested the presence of a cyclopropane group. This assumption was further substantiated by a band at  $3080\text{ cm}^{-1}$  in the IR spectrum. The  $^{13}\text{C}$  NMR spectrum not only shows the absence of  $\text{sp}^2$  carbon atoms but also the presence of four  $\text{CH}_3$  (45.11; 45.37; 53.85 and 61.49 ppm), five  $\text{CH}_2$  (31.71; 36.44; 44.72; 50.81 and 53.14 ppm), three CH (20.84; 26.79 and 56.15 ppm) and three C (-10.22; 42.52 and 58.58 ppm) <sup>(5)</sup>.

Africanol is thus a tricyclic monohydroxylated sesquiterpene. All our attempts to correlate the carbocyclic ring system of africanol with one of the already known sesquiterpene skeleton have failed. Under a variety of conditions africanol affords either a low yield of unsaturated hydrocarbons (*vide infra*) or complex mixtures of untractable products.

The compound was thus submitted to single crystal X-ray diffraction analysis which led to structure (I) - relative configuration. The compound crystallises in the orthorhombic system, space group  $P 2_1 2_1 2_1$  with  $a = 29.47 \text{ \AA}$ ,  $b = 18.08 \text{ \AA}$  and  $c = 9.71 \text{ \AA}$ . The unit cell contains twelve molecules <sup>(6)</sup>.



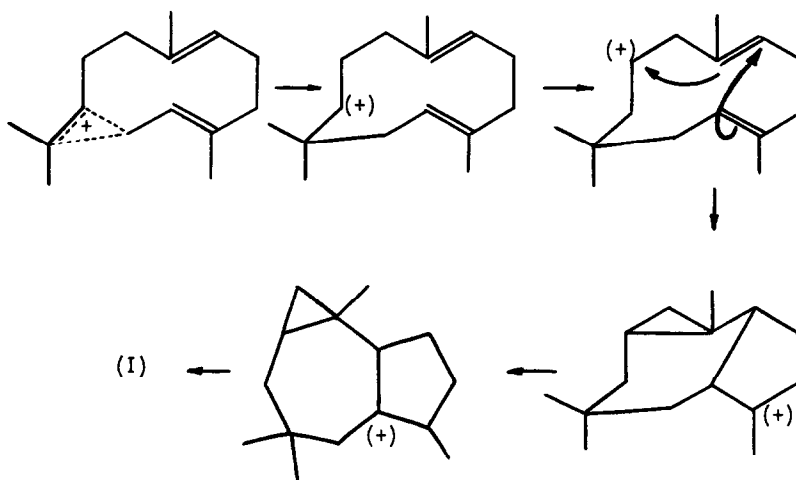
I



II

When africanol is submitted to dehydration conditions ( $\text{POCl}_3$  or  $\text{SOCl}_2$  in pyridine) or to acid treatment (formic or hydrochloric acid), a complex mixture is formed from which a fraction containing three isomeric  $\text{C}_{15}\text{H}_{24}$  unsaturated hydrocarbons is isolated <sup>(7)</sup>. One of these (UV ( $\text{CH}_3\text{OH}$ ) : end absorption; IR : no  $\nu_{\text{OH}}$  band; NMR ( $\text{CCl}_4$ ): three  $-\text{C}-\text{CH}_3$  groups at 0.86, 0.86 and 0.91 ppm; one  $\text{CH}_3-\text{C}=\text{C}$  group at 1.66 ppm and two of the cyclopropanic protons between 0.1 and 0.6 ppm) could be separated by repetitive chromatography on silicagel columns impregnated with 10 %  $\text{AgNO}_3$ . All these data strongly point to structure II for this unsaturated hydrocarbon. From the spectroscopic data obtained on the original mixture of isomers, it is highly probable that the two remaining unsaturated hydrocarbons are the two other possible dehydration products of africanol.

Africanol is the first representative of a new type of tricyclic sesquiterpene the formation of which could be visualized as shown hereunder.



The chemical structure of other alcyonarian terpenoids as well as their biological significance is currently under investigation in our laboratory.

REFERENCES

- (1) Part VII. J.Org.Chem. 35, 2585 (1970).
- (2) a. P.J.SCHEUER "Chemistry of marine natural products" Ed. Ac. Press 1973.  
b. A.J.WEINHEIMER, F.J.SCHMITZ and L.S.CIERESZKO "Drugs from the sea" p. 135  
Transactions of the Drugs from the Sea Symposium ; Marine Technology Society ;  
University of Rhode Island (1967).  
c. E.PREMUZIC "Chemistry of natural products derived from marine sources" in  
Progress in the Chem. of Org. Nat. Products Vol. XXIX, (1971).
- (3) This is a part of the comprehensive collection of Indonesian alcyonarians effected  
by Mr. J.PIERRET, whose contribution we gratefully acknowledge.
- (4) 60 MHz,  $\text{CDCl}_3$ , values in ppm from internal TMS.
- (5) 22.63 MHz,  $\text{CDCl}_3$ , positive values in ppm are upfield from internal  $\text{CDCl}_3$ .
- (6) A full paper on the X-ray work will appear shortly.
- (7) The same mixture of hydrocarbons is also present in the animal.

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