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STEREOCHEMISTRY OF DIHYDROAGAROFURANS AND EVIDENCE IN SUPPORT OF THE STRUCTURE OF 4,11-EPOXY-CIS-EUDESMANE

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The current interest in the search for attractants and trail following substances had led to the isolation of dihydroagarofuran from the West-Indian Sandalwood oil[1] and 4,11-epoxy cis-eudesmane from the frontal gland secretion of the termite Amitermes evuncifer silvestri.[2] This communication deals with the stereochemistry of these compounds.

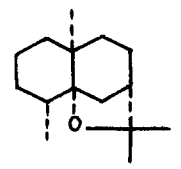
Maheshwari et al.[3], demonstrated the identity of natural dihydroagarofuran (I) with the hydrogenation product of β-agarofuran (II). Since the stereostructure of (II) was later modified[4] to (III), the dyhydro-β-agarofuran is considered to be (IV).

We have recently shown that one of the microbial oxidation products of valencene (V) is identical with dihydro-α-agarofuran[5]. Since the stereochemistry at C-4 of valencene (V) is settled beyond doubt[6], the previously assigned[3] stereochemistry at C-4 of natural dihydroagarofuran and consequently dihydro α and β-agarofurans is in error and must be as shown in (IV) & (VI) respectively.

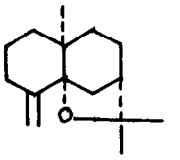
Ritter et al., reported the isolation of dihydroagarofuran from sandalwood oil[1] but did not make a definite stereochemical assignment. A direct spectral comparison (i.r., n.m.r.) established its identity with dihydro-β-agarofuran (VI).

Recently, structure (VII) has been assigned to the sesquiterpene isolated from the frontal gland of the termite A. evuncifer.[2] An interesting feature of the structural studies is the formation of dihydroagarofuran (identical with Ritter's dihydroagarofuran) as one of the products on treatment of (VII) with BF_3-etherate. Since Ritter's dihydroagarofuran is (VI), its stereospecific

formation from (VII) can be explained via the carbonium ion (VIII) by a 1,2 hydride shift followed by ring closure. Wadhams' sesquiterpene ether must therefore be (IX) or its mirror image as suggested[2].



I



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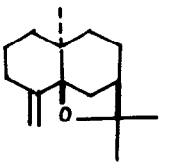

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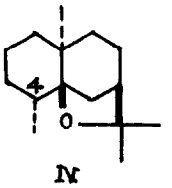
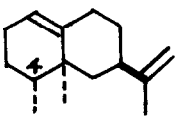
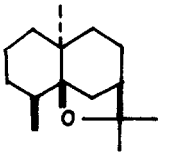


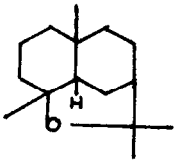
IV



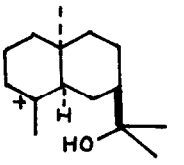
V



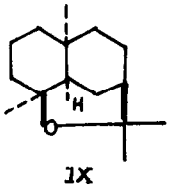
VI



VII



VIII



IX

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