Tetrahedron Letters No.20, pp. 2497-2500, 1968. Pergamon Press. Printed in Great Britain.

STRUCTURAL RELATIONSHIPS BETWEEN TRICYCLIC SESQUITERPENES IN OILS OF VETIVER (1)

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(Received in USA 27 December 1967; accepted for publication 19 February 1968)

The isolation and structure of three sesquiterpenes, possessing a novel carbon-skeleton, khusenic acid (I), isokhusenic acid (IV) and khusenol (II) from Angola vetiver oil have been reported in recent communications from this laboratory (2-4). In the previous literature two types of tricyclic sesquiterpenes occurring in vetiver oils have been described. Tricyclovetivenol (V) and tricyclovetivene (VI) were isolated from Congo vetiver oil (5,6), and khusimol (VII) was isolated from South Indian vetiver oil (7). A sesquiterpene hydrocarbon, khusimene (VIII), was obtained from Japanese vetiver oil and was shown to be related to khusimol (8). Zizanoic acid, isolated recently from Japanese vetiver oil, was assigned the same structure as khusenic acid (9). Comparison of the properties of these acids and their degradation products indicates their identity. This communication summarises recent investigations which show that the acids, alcohols and hydrocarbons referred to possess the same carbon-skeleton, viz. that assigned to khusenic acid (I).

Vetiver oils of several origins including Congo and South India were used. The acids were isolated as methyl esters employing Amberlite IRA-400 ion exchange resin (2,10) and the acid-free oils were treated with Girard T. Reagent to separate aldehydes and ketones (11). The remaining oils yielded the primary alcohol fractions on phthalic anhydride treatment (12). Gas chromatographic examination of the ester and alcohol fractions, as previously described (2,4), suggested that their major constituents were methyl khusenate and khusenol, respectively. In order to confirm that khusenol, tricyclovetivenol and khusimol are, in fact, identical small

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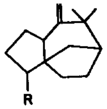
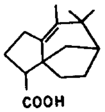
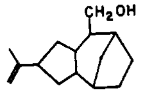


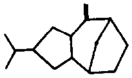
I , R = COOH
II , R = CH_2OH
III , R = CH_3



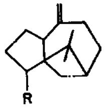
IV



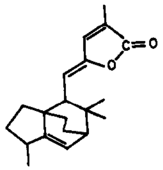
V



VI



VII , R = CH_2OH
VIII , R = CH_3



IX

quantities of the main constituents present in the primary alcohol fractions of Congo and South Indian oils were prepared by column (alumina) and gas chromatography. The infrared spectra of these two isolates, of natural khusenol (ex Angola vetiver oil), and of synthetic khusenol ($LiAlH_4$ reduction of methyl khusenate) agreed with one another and with those of tricyclovetivenol and khusimol published in literature (5-7). The NMR spectra of these alcohols were also identical (Table I). Oxidation of khusenol, tricyclovetivenol and khusimol with Jones' reagent (13) yielded acids which, after purification via their cyclohexylamine salts, were obtained as semisolid substances. The acids failed to crystallise but their infrared and mass spectra were identical with those of khusenic acid (2). Tricyclovetivenol, khusimol and khusenol, are therefore, the same compound.

Table I

NMR Data for Alcohols from Vetiver Oils

(Chemical shifts in ppm downfield from TMS in $CDCl_3$)

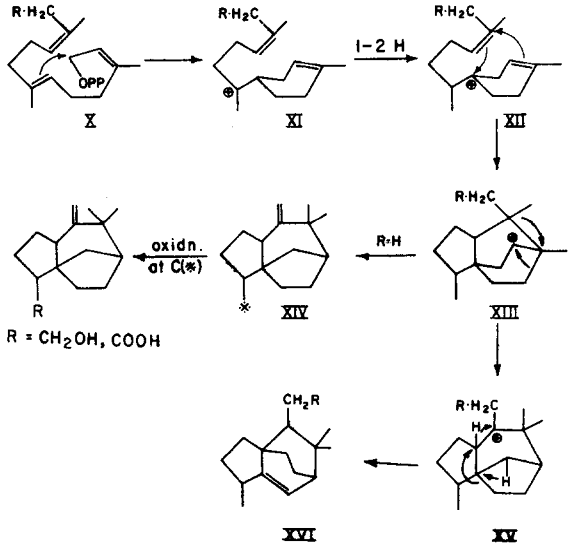
Sample	Origin	Methyl Protons	Olefinic Protons*
Khusenol	Angola vetiver oil	1.07, 1.06**(6H)	4.58, 4.73 (2H)
Khusenol	$LiAlH_4$ reduction of methyl khusenate	1.07, 1.06**(6H)	4.62, 4.75 (2H)
Tricyclovetivenol	Congo vetiver oil	1.07, 1.06**(6H)	4.62, 4.75 (2H)
Khusimol	South Indian vetiver oil	1.07, 1.05**(6H)	4.60, 4.74 (2H)

* peaks observed as triplets (centered at the positions recorded) apparently due to long range coupling, J = 1.7 cps.

** observed as a shoulder.

These findings necessitated a re-examination of the structures assigned to tricyclovetivene (VI) (6) and khusimene (VIII) (8). A sample of khusene (III) was prepared by tosylation and $LiAlH_4$ reduction of khusenol, obtained from methyl khusenate. As expected its infrared spectrum was identical with that of khusimene (8) and resembled closely that of tricyclovetivene (6). Since Chiurdoglu has reported the relationship between tricyclovetivenol and tricyclovetivene (5) and we have established the identity of tricyclovetivenol and khusenol, it may be concluded that tricyclovetivene, khusene and khusimene are identical.

The khusane carbon skeleton is of biosynthetic interest as it represents a novel sesquiterpene framework. It has been proposed (3a,9) that the carbonium ion XI (R = H) derived from farnesyl pyrophosphate (X, R = H) can yield khusene, khusenic acid and khusenol - see Scheme I (3). According to Hendrickson (14), this ion is also an intermediate in the biosynthesis of cedrol, and of α- and β-cedrene. Formation of the diterpene eremolactone (IX), whose structure was recently established (15,16), may take place in accordance with a similar scheme. The intermediate XIII [$R = -CH_2-CH{=}C(CH_3)_2$] would be expected to yield the eremolactone carbon skeleton (XVI) *via* the cation XV.



Scheme I

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