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THE CONSTITUENTS OF THE VOLATILE OIL FROM THE WOOD OF TORREYA NUCIFERA.

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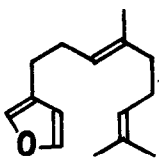
Four new sesquiterpenes together with dendrolasin and o-methoxycinnamic aldehyde were isolated from the neutral volatile wood oil of Torreya nucifera Sieb. et Zucc. by adsorption chromatography on silica gel.

The first eluate, pure dendrolasin (I) was isolated previously from the ant Lasius (Dendrolasius) fulginosus Latr. by Quilico et al.[1] and from the sweet potato fusel oil in our laboratory.[2]

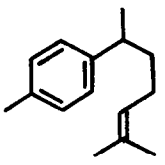
From the second fraction an aromatic sesquiterpenic aldehyde, $C_{15}H_{20}O$, was isolated for which we propose the name nuciferal. It had b.p.107·5-108·5°/0·03mm.; $[\alpha]_D^{20}$ + 62·07° (c=16·547 in $CHCl_3$). ($\lambda_{max.}^{EtOH}$ in mμ (ε): 222·5(15,700); 229(14,730); 264·5(950); 266·5(880); 273(800); 279·5(370). $\nu_{max.}^{liq.}$ in cm.$^{-1}$: 2720(CHO); 1690 (conj. C=O); 1645(C=C); 1519, 818(aromatic).) Its 2,4-dinitrophenylhydrazone has m.p. 138-139°. (Found: C, 63·60; H, 6·06; N, 14·04. Calc. for $C_{21}H_{24}N_4O_4$: C, 63·62; H, 6·10; N, 14·13.) The Kishner reduction of the semicarbazone of nuciferal yields an aromatic hydrocarbon, identical in respect of IR spectra and retention times of gas chromatography with natural ar-curcumene (II) isolated from ginger oil. As both the IR and UV spectra show that nuciferal is an α,β-unsaturated aldehyde, 2-methyl-6(p-tolyl)hepten-2-al-1 (III) has been suggested as the structure.

A β-furanoid sesquiterpenic aldehyde, $C_{15}H_{20}O_2$, was eluted after the

nuciferal fractions. It has been named torreyal and has b.p. 124-126°/0·05 mm.; $[\alpha]_D^{20}$ +1·90°. ($\lambda_{max.}^{EtOH}$ in mμ(ε): 224(15,940). $\nu_{max.}^{liq.}$ in cm.$^{-1}$: 2720(CHO); 1690 (conj. C=O); 1645(C=C); 1570, 1504, 1164, 1028, 874, 779(furan).) Its 2,4-dinitrophenylhydrazone has m.p. 111-112°. (Found: C, 61·32; H, 5·83; N, 13·58. Calc. for $C_{21}H_{24}N_4O_5$: C, 61·15; H, 5·87; N, 13·59). The Kishner reduction of the semicarbazone of torreyal yields dendrolasin. On ozonolysis of torreyal, levulinic aldehyde was isolated as its bis-2,4-dinitrophenylhydrazone (m.p.238°). As no acetone was detected, the structure of torreyal was concluded to be 2,6-dimethyl-9(3-furyl)nonadien-2,6-al-1 (IV).



I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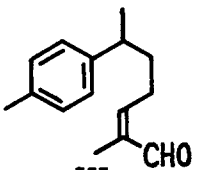
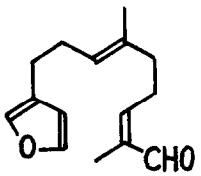
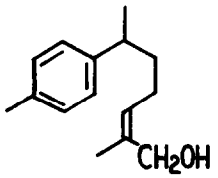


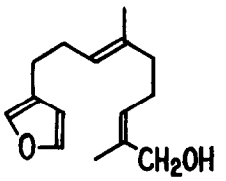
III



IV



V



VI

From the fourth fraction, an aromatic sesquiterpenic alcohol, $C_{15}H_{22}O$, b.p. 131-132°/ 0·05 mm; $[\alpha]_D^{20}$ +41·06° was isolated. ($\lambda_{max.}^{EtOH}$ in mμ (ε): 252·5(374); 259(478); 264·5(570); 276·5(560); 273(622). $\nu_{max.}^{liq.}$ in cm.$^{-1}$: 3340(OH); 1518, 819 (aromatic).) It was oxidized to nuciferal by chromic acid and the original alcohol was regenerated by the reduction of nuciferal with $LiAlH_4$. Hence, this compound is the alcohol corresponding to nuciferal and is named nuciferol (V).

From the fifth fraction, a β-furanoid sesquiterpenic alcohol, $C_{15}H_{22}O_2$, b.p. 117-119°/ 0·03 mm.; $[\alpha]_D^{20}$ ± 0°., was isolated. As it is identical with

the $LiAlH_4$ reduction product of torreyal, this compound must be the corresponding alcohol of torreyal. Previously, the sesquiterpenic alcohol isolated from the leaves of Torreya nucifera was named "torreyol" by Shonozaki[3], although this alcohol was proved by us to be identical with δ-cadinol[4]. We propose to name this β-furanoid sesquiterpenic alcohol, torreyol (VI) based on the evidence described in this communication.

The last fraction was o-methoxycinnamic aldehyde, m.p.45-46°.

REFERENCES

1 A. Quilico, F. Piozzi and M. Pavan, Tetrahedron 1, 177 (1957).

2 Y. Hirose, M. Abu and Y. Sekiya, Nippon Kagaku Zasshi 82, 725 (1961).

3 E. Shinozaki, Nippon Kogyokagaku Zasshi 25, 768 (1922).

4 T. Sakai, H. Chikamatsu and Y. Hirose, Presented at the 6th Symposium on Perfumes, Terpenes and the Chemistry of Essential Oils, Chem. Soc. Japan, Aug. 1962, at Ina, Abstracts pp. 1.