Phytochemistry, 1970, Vol. 9, pp. 2419 to 2422. Pergamon Press. Printed in England.

SHORT COMMUNICATION

NOOTKATENE FROM *CITRUS SINENSIS*

ERIC D. LUND, RICHARD L. COLEMAN and MANUEL G. MOSHONAS

U.S. Fruit and Vegetable Products Laboratory, Winter Haven, Florida, U.S.A.*

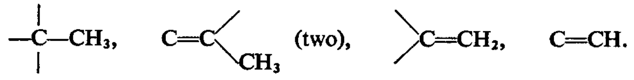
(*Received* 24 *February* 1970)

Abstract—The sesquiterpene hydrocarbon nootkatene and an unidentified sesquiterpene hydrocarbon, MW 204, have been isolated from Valencia orange peel.

RESULTS AND DISCUSSION

IN CONJUNCTION with the isolation of large quantities of the sesquiterpene hydrocarbon valencene from Valencia orange peel oil, we have isolated two sesquiterpene hydrocarbons. The two compounds, which had not been previously characterized in studies on this fraction,[1-3] were separated from valencene by GLC on Carbowax 20M. The first of these had a retention time of 38 min, slightly larger than valencene (36 min), and the second a retention time of 40 min.

The first unknown appeared as a small peak immediately after valencene in the GLC and, due to the insufficient quantity available, could not be completely characterized. The m.s. of this unknown indicated an MW of 204 (Fig. 2). The i.r. spectrum (Fig. 2) had strong bands at 1650 and 895 cm^{-1} typcial of C—C double bonds. The u.v. spectrum showed only end absorption. The NMR spectrum in CCl_4 had the following strong signals: $\delta = 0{\cdot}85$ (singlet) 3H, 1·59 (singlet) 3H, 1·73 (singlet) 3H, 4·83 (singlet), 2H, 5·24 (broad peak) 1H (ppm relative to TMS). From the NMR spectrum, the following structural features were indicated:



Hydrogenation of the unknown produced a saturated hydrocarbon, MW 208 (m.s.). The i.r. spectrum of the unknown and its saturated derivative did not correspond to any of the known sesquiterpene hydrocarbons according to Ourisson *et al.*[4]

The second compound, which was pure according to GLC analysis on both Carbowax 20M and SE-30, had MW 202, according to mass spectral analysis (Fig. 1). The i.r. spectrum (Fig. 1) of the unknown was characteristic of an unsaturated hydrocarbon with a strong

---

* One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

Mention of brand names does not imply endorsement.

[1] R. TERANISHI, T. H. SCHULTZ, W. H. MCFADDEN, R. E. LUNDIN and D. R. BLACK, *J. Food Sci.* **28**, 541 (1963).

[2] G. L. K. HUNTER and W. B. BROGDEN, JR. *J. Food Sci.* **30**, 1 (1965).

[3] G. L. K. HUNTER and W. B. BROGDEN, JR. *J. Food Sci.* **30**, 383 (1965).

[4] G. OURISSON, S. MUNAVALLI and C. EHRET, *International Tables of Selected Constants*, 15, *Data Relative to Sesquiterpenoids*, Pergamon Press, Oxford (1966).

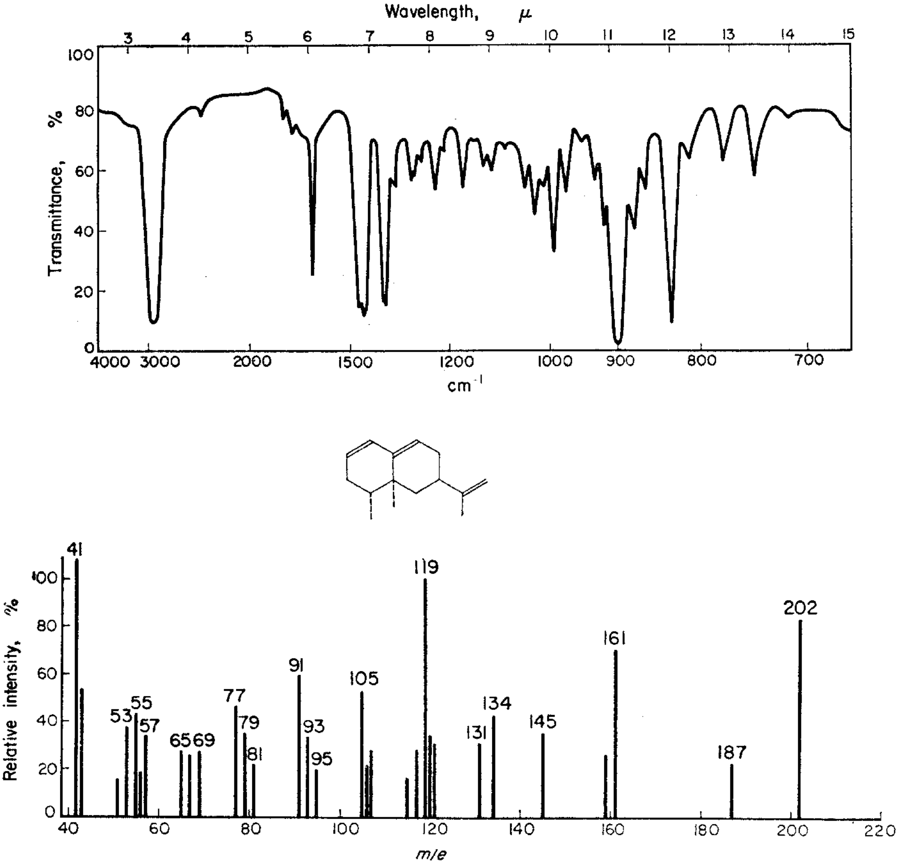
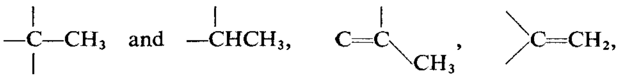


FIG. 1. I.R. AND MASS SPECTRA OF NOOTKATENE.

band at 1650 cm^{-1} and strong bands at 2900, 1440–1460, 1380, 900, and 830 cm^{-1} (r The u.v. spectrum λ_{max}^{EtOH} 235 log ξ 1·12 and 228 log ξ 1·09, demonstrates the presence of substituted conjugated diene. The NMR spectrum in CCl_4 had signals at $\delta = 0{\cdot}90$ (si and doublet) 6H, 1·75 (singlet) 3H, 4·73 (singlet) 2H, and a complex multiplet at 5·2–6·0 (The following structural features are deduced from the NMR:



$$-\overset{|}{\underset{|}{C}}-CH_3 \text{ and } -\overset{|}{C}HCH_3, \quad C{=}\overset{|}{C}\diagdown_{CH_3}, \quad \rangle C{=}CH_2,$$

and 3 protons on conjugated double bonds. Hydrogenation of the unknown yielded a rated hydrocarbon, MW 208 (m.s.) identical in i.r. spectrum to the saturated hydroca 4βH-nootkatane,[5] obtained by hydrogenation of valencene under the same conditions. unknown was, therefore, a triene based on the nootkatane skeleton and the data sugg that it was nootkatene (4βH-nootkata-1,9,11-triene).[6,7] An authentic sample of nootka synthesized from nootkatone according to the procedure of MacLeod,[7] had MW 202 ar i.r. spectrum identical with that of the unknown (see Fig. 1).

[5] N. H. ANDERSEN and M. S. FALCONE, *J. Chromatog.* **44**, 52 (1969).
[6] H. ERDTMAN and J. G. TOPLISS, *Acta Chem. Scand.* **11**, 1157 (1957).
[7] W. D. MACLEOD, JR. *Tetrahedron Letters* 4779 (1965).

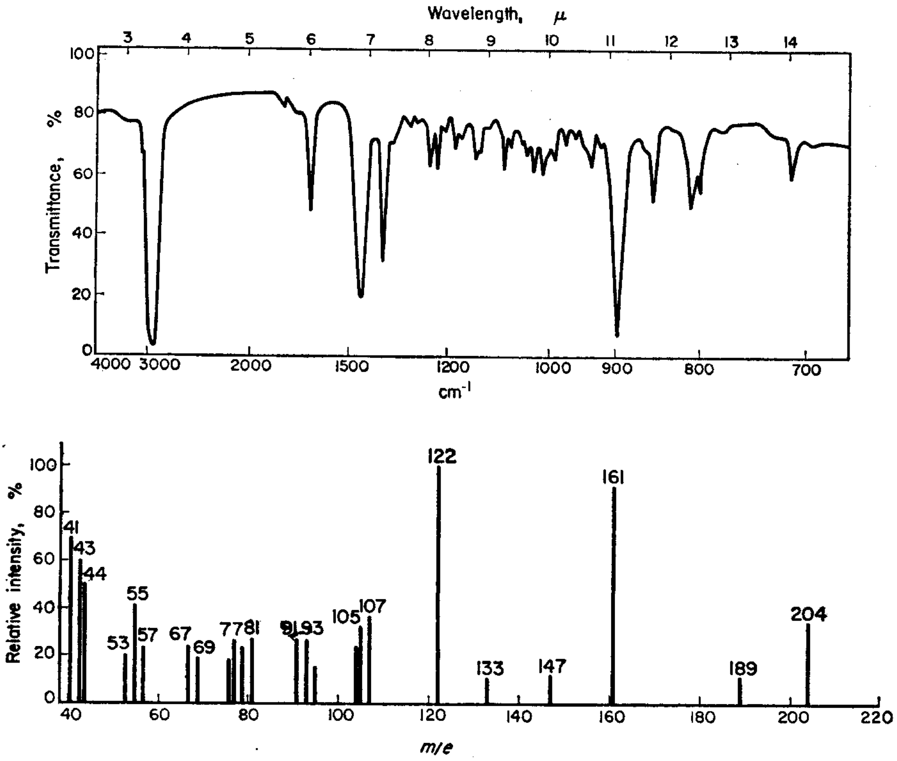


FIG. 2. I.R. AND MASS SPECTRA OF UNIDENTIFIED SESQUITERPENE HYDROCARBON.

EXPERIMENTAL

Spectroscopic Measurements

Mass spectra were obtained with a Bendix Model 3012 Time-of-Flight mass spectrometer operating at 70 eV.

GLC

The two hydrocarbons were separated from valencene by GLC on a 610 cm × 1 cm I.D. aluminum column packed with 20% Carbowax 20M on 60/80 acid-washed Chromosorb W, with the column programmed from 150° to 220° at 2°/min and helium flow rate of 200 ml/min. The injector port temp. was 266° and the thermal conductivity detector temp. was 260°. Injection volume was 400 μl.

The impurity of each of the hydrocarbons was checked by GLC on a 610 cm × 0·33 cm I.D. aluminum column packed with 5% SE-30 on 70/80 acid-washed Chromosorb W, with the column programmed from 150° to 250° at 1°/min and a helium flow rate of 30 ml/min. The injector port temp. was 250°. Detection was by means of a flame ionization detector at 330°. Injection volume was 1 μl of a 10% solution in ether. Under these conditions the retention time of nootkatene was 25 min and that of the first unknown was 27 min.

Hydrogenation

Reduction to the saturated hydrocarbons was carried out by hydrogenation with PtO_2 in ethanol at 60 psi for 2 hr. Data on the reduced product were obtained from the unpurified hydrogenation product.

Synthesis of Nootkatene

Nootkatene was synthesized from nootkatone according to the three-step sequence described by MacLeod,[7] and the reactions carried out by the procedures described in the references cited therein. The final product was purified by GLC on a 610 cm × 0·66 cm I.D. aluminum column packed with 20% SE-30 on 60/80 acid-washed Chromosorb W, with the column programmed from 150° to 230° at 1·5°/min and a helium flow rate of 45 ml/min. The injector port temp. was 250° and the thermal conductivity detector temperature was 280°. Injection volume was 200 μl of a 10% solution in ether. Under these conditions the retention time of nootkatene was 59 min.

Acknowledgement—The authors express appreciation to Dr. Harold E. Nordby for the NMR data.