Phytochemistry, 1968, Vol. 7, pp. 1419 to 1420. Pergamon Press. Printed in England

SHORT COMMUNICATION

n-ALKANES OF THE ENGLISH "OAK APPLE"

D. H. CALAM*

National Institute for Medical Research, Mill Hill, London, N.W.7,
and Rothamsted Experimental Station, Harpenden, Herts. (Present address)

(*Received* 21 *February* 1968)

Abstract—From the "oak apple", the gall produced by *Biorhiza pallida* (Olivier), a mixture was isolated (0·42 per cent) consisting of all the saturated, straight-chain alkanes from $C_{18}H_{38}$ to $C_{31}H_{64}$. The main components are the C_{25} (42 per cent), C_{27} (22 per cent), C_{23} (18 per cent) and C_{29} (16 per cent) compounds.

INTRODUCTION AND DISCUSSION

THE SPONGY, red-tinted galls ("oak apples") produced by the gall wasp *Biorhiza pallida* (Olivier) are commonly observed on oak trees in late spring in England. In the course of an investigation of these galls for the presence of a substance with specific physiological activity, chromatography of the light petroleum extract on alumina yielded a white wax, m.p. 53–55°. I.r. and NMR spectroscopy and elementary analysis indicated the presence of only a single chemical species, but gas chromatography showed it to be a complex mixture. On the basis of gas chromatographic retention times and analysis by combined gas chromatography and mass spectrometry, the components of the mixture were identified as the series of normal alkanes $C_{18}H_{38}$ to $C_{31}H_{64}$ with the four odd-carbon numbered members C_{23}, C_{25}, C_{27} and C_{29} comprising 98 per cent of the total.

This gall does not seem to have been studied chemically before and the alkane composition of other oak galls and the oak leaf itself are unknown. However, the composition of the oak apple alkane mixture is probably slightly unusual among those obtained from plant sources in having n-$C_{25}H_{52}$ as the main constituent, because the range C_{27}—C_{33} is more common.[1,2]

EXPERIMENTAL

The galls were collected in May 1965 and stored at −5° until used in February 1966. The galls (270 g) were minced and extracted with light petroleum (b.p. 60–80°) in a Soxhlet for 12 hr. The extract was dried (Na_2SO_4) and evaporated to a gum (9·5 g, 3·5 per cent). This was chromatographed as a light petroleum solution on alumina (150 g, Brockmann activity III). Elution with light petroleum (100 ml) gave a white wax (Fraction 1, 1·140 g).

Fraction 1 was crystallized from ethanol as white flakes (429 mg), m.p. 53–55°. (Found: C, 85·1 84·8; H, 14·6, 14·6 per cent). The i.r. spectrum indicated a saturated hydrocarbon, the NMR spectrum (CCl_4 solution) showed only signals expected for normal hydrocarbons and an average composition approximately $C_{24}H_{50}$. The solid was further examined as a hexane solution by gas chromatography using a Perkin-Elmer

[1] G. EGLINTON, R. J. HAMILTON and M. MARTIN-SMITH, *Phytochem.* **1**, 137 (1962).
[2] G. EGLINTON and R. J. HAMILTON in *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 187. Academic Press, London (1963).

F11 instrument with a flame ionization detector and helium as carrier gas at 5 lb/in^2. Samples were chromatographed on a 2m × $\frac{1}{8}$ in. column packed with 1$\frac{1}{2}$ per cent E-301 silicone gum rubber on AW-DMCS Chromosorb W, at oven temperatures from 210 to 242°. For mass spectrometry, part of the column effluent was taken through a heated capillary and Watson-Biemann separator into a Hitachi Perkin-Elmer RMU-6E mass spectrometer operated at a chamber temperature 220° and ionization voltage 80 eV. Mass spectra were taken of individual components of the mixture as they emerged from the gas chromatograph. None showed evidence of chain branching. The relative composition of the mixture was determined from gas chromatographic traces by triangulation and is given in Table 1. The C_{22} to C_{29} compounds (inclusive) were identified from their mass spectra; the identity of the other, minor, components was inferred from retention time data.

TABLE 1. COMPOSITION OF THE ALKANE MIXTURE FROM OAK APPLES

Carbon number	Log retention time (242°)	Percentage
C_{16} standard	0·17	—
C_{18}	0·38	0·007
C_{19}	0·46	0·012
C_{20}	0·52	0·018
C_{21}	0·61	0·062
C_{22}	0·73	0·15
C_{23}	0·85	18
C_{24}	0·97	1·1
C_{25}	1·10	42
C_{26}	1·22	0·64
C_{27}	1·36	22
C_{28}	1·46	0·55
C_{29}	1·62	16
C_{30}	1·79	0·12
C_{31}	1·89	0·21

Acknowledgement—I thank Dr. R. K. Callow, F.R.S. for the oak galls and Dr. N. F. Janes for the NMR spectrum.