

COMPONENTS OF PLANTS OF THE EMPETRACEAE FAMILY.

III. CYCLOALKANES FROM *Empetrum nigrum*

N. N. Red'kina, O. V. Bryanskii, E. A. Krasnov,
A. A. Semenov, and E. V. Ermilova

UDC 547.21:543:544:621.384.8

We have continued an investigation of the lipophilic extracts of crowberry and have established that, in addition to paraffins [1], they contain macrocyclic alkanes.

The nonpolar fraction obtained by column chromatography of the hexane extract of black crowberry *Empetrum nigrum* L. (SiO_2 , hexane, chloroform, and ethanol in various ratios) followed by rechromatography (SiO_2 , hexane, chloroform) was subjected to further purification by preparative reversed-phase chromatography [Silasorb C., tetrahydrofuran-water (7:3)]. A colorless chromatographically homogeneous substance was obtained with a yield of 0.02% on the absolutely dry epigeal mass, mp 78-82°C, sparingly soluble in the majority of organic solvents. The IR spectrum (UR-20 spectrometer, $\nu_{\text{max}}^{\text{KBr cm}^{-1}}$) had absorption bands at 2900, 2825, and 1450 (ν sym. and asym., δ sym. of CH_2). In the ^1H and ^{13}C NMR spectra recorded on a XL-100 instrument (Varian) at 50°C in deuterochloroform (δ , ppm, 0 - TMS) one signal was recorded in each case (1.26 and 29.7 ppm, respectively). Mass spectrometric fragmentation gave the pattern typical for alkanes [2].

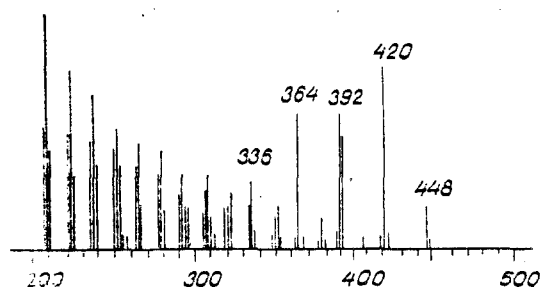


Fig. 1. Mass spectrum of cycloalkanes (region of molecular ions).

Clusters separated by an interval of 14 m.u. and decreasing uniformly in intensity but no other fragments whatever were observed. In the region of molecular ions the uniformity of the decrease in intensity was disturbed, as can be seen from Fig. 1.

On the basis of these facts we concluded that the substance isolated consisted of a mixture of cycloalkanes with molecular masses of 336, 364, 392, 420, and 448: $\text{C}_{24}\text{H}_{48}$ - cyclo-tetracosane; $\text{C}_{26}\text{H}_{52}$ - cyclohexacosane; $\text{C}_{28}\text{H}_{56}$ - cyclooctacosane; $\text{C}_{30}\text{H}_{60}$ - cyclotriacontane; and $\text{C}_{32}\text{H}_{64}$ - cyclodotriacontane.

It is striking that while in the mixture of paraffins from the crowberry compounds with odd numbers of carbon atoms, C_{31} , C_{29} , and C_{33} predominate, the macrocyclic alkanes are represented by substances with even numbers of carbon atoms.

This is the first time that the cycloalkanes that we have obtained have been isolated from plants. Some of these macrocyclic hydrocarbons have been synthesized previously [3, 4].

LITERATURE CITED

1. E. V. Ermilova, E. A. Krasnov, and G. Z. Khanin, Khim. Prir. Soedin., 598 (1987).
2. I. G. Zenkevich and B. V. Ioffe, The Interpretation of the Mass Spectra of Organic Compounds [in Russian], Leningrad (1986).

Tomsk Medical Institute. Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 719-720, September-October, 1989. Original article submitted October 24, 1988; revision submitted May 22, 1989.

3. F. Sondheimer and R. Wolovsky, J. Am. Chem. Soc., 84, 260 (1962).
4. F. Sondheimer and J. Gaoni, J. Am. Chem. Soc., 81, 6301 (1959).

NEUTRAL LIPIDS OF BARK OF THE ROOTS OF *Maclura aurantica*

N. A. Artamonova, G. I. Krotova, G. K. Nikonov,
and V. V. Kiseleva

UDC 547.915:543.544

The air-dry comminuted bark of the roots (4 kg) of osage orange was extracted with petroleum ether (40-70°C). When the extract was evaporated, yellow crystals deposited with mp 182-183°C, composition $C_{23}H_{22}O_6$, which, on the basis of their IR, UV, and PMR spectra, were identified as 12-(1,1-dimethylallyl)-5,9,10-trihydroxy-2,2-dimethyl-2H,6H-pyrano[3,2-b]xanthen-1-one (macluraxanthone); yield 0.04% [1].

On further evaporation of the extracts, lipids were obtained in the form of a viscous yellow liquid (25 g). When the lipids (5 g) were saponified with a 0.5 N solution of KOH in methanol, two fractions were obtained: unsaponifiable (1) and saponifiable (2).

Fraction 1 was deposited on a column of KSK silica gel (0.16-0.20 mm). When the column was washed with petroleum ether, a fraction was obtained with mp 55-57°C in a yield of 0.008% (on the dried weight of the bark) which consisted of the sum of the hydrocarbons, and its qualitative and quantitative compositions were studied by gas-liquid chromatography on a Chrom-5 instrument. GLC conditions: glass column 0.4 × 250 cm, filled with 10% of diethyleneglycol succinate on Chromaton NAW (0.20-0.25 mm) at a column temperature of 204°C and an evaporator temperature of 250°C. Hydrocarbons were identified from their retention times with markers [2, 3]. Composition of the hydrocarbons (5): $C_{10:0}$ - 0.1; $C_{12:0}$ - 0.3; $C_{14:0}$ - 0.2; $C_{15:0}$ - 0.6; $C_{16:0}$ - 0.3; $C_{18:0}$ - 0.2; $C_{20:0}$ - 0.8; $C_{21:0}$ - 0.7; $C_{22:0}$ - 0.8; $C_{23:0}$ - 0.5; $C_{24:0}$ - 0.4; $C_{25:0}$ - 1.7; $C_{26:0}$ - 1.1; $C_{27:0}$ - 35.5; $C_{28:0}$ - 7.1; $C_{29:0}$ - 49.7. The main hydrocarbons of the bark of the root of osage orange are heptacosane, octacosane, and nonacosane, which together amount to 92.3%. When the column was washed with petroleum ether-ethyl acetate (3:1) a substance was isolated with mp 190-191°C (melting point of the acetate 205-206°C), which was identified by IR, UV, and PMR spectroscopy as lupeol; yield 0.0007% (on the dry weight of the bark).

When the concentration of ethyl acetate in the eluting mixture was increased further, prenylated xanthenes were isolated: tovoxanthone (0.006%), 6-deoxyjacareubin (0.001%), macluraxanthone (0.06%), and alvaxanthone (0.02%) [4]. IR, UV, and PMR spectroscopies were used to establish the structures of the xanthenes.

Fraction 2 was methylated [5] and analyzed by GL on a column (see above) at a temperature of 180°C. Composition of the fatty acids (%): $C_{9:0}$ - 0.6; $C_{14:0}$ - 1.8; $C_{15:0}$ - 0.6; $C_{15:1}$ - 0.1; $C_{16:0}$ - 36.7; $C_{16:1}$ - 0.6; $C_{18:0}$ - 1.6; $C_{18:1}$ - 28.3; $C_{18:2}$ - 5.8; $C_{18:3}$ - 23.9. The main acids from the root bark were palmitic, oleic, and linolenic. The qualitative composition of the root fatty acids is analogous to the fatty acid composition of the fatty oil from the fruit [6]. Thus, the neutral lipids of the bark of osage orange roots form a complex combination of substances which includes hydrocarbons, fatty acids, the tri-terpene alcohol lupeol, and prenylated xanthenes. We are first to have shown the presence of these components in the lipids.

LITERATURE CITED

1. M. L. Wolfrom, F. Komitsky, J. G. Fraenkel, et al., J. Org. Chem., 29, No. 3, 692 (1964).
2. M. Kates, Techniques of Lipidology, American Elsevier, New York (1972).

Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata. Translated from Khimiya Prirodnikh Soedinenii, No. 5, pp. 720-721, September-October, 1989. Original article submitted January 9, 1989; revision submitted April 11, 1989.