Tetrahedron Letters No.14, pp. 1669-1673, 1968. Pergamon Press. Printed in Great Britain.

SIMPLIFICATION OF COMPLEX MIXTURES OF ALKANES USING A 7A MOLECULAR SIEVE

R. Curran, G. Eglinton,* I.Maclean,
(Department of Chemistry, The University, Glasgow)
A. G. Douglas, and G. Dungworth,
(Organic Geochemistry Unit, Geology Department, The University, Newcastle-upon-Tyne).

(Received in UK 29 November 1967)

Extraction of organic material from both biological and geological sources gives rise to extremely complex mixtures (1). Identification and/or isolation of single components is difficult. Even after resolution by standard techniques into the different chemical classes, a further simplification of the still complex mixture is necessary. This may be achieved by use of properties, such as volatility, partition coefficients, adsorption characteristics etc., or of properties largely dependent on molecular size, e.g. clathration (2,3,4) and molecular sieving (5).

The urea adduction technique has been extended by the use of thiourea, whose crystal lattice contains channels of approximately 7Å diameter. Thiourea adduction has been used (6) to separate acyclic isoprenoid hydrocarbons (such as pristane and phytane) and cyclic hydrocarbons which have a long branched side chain (such as ergostane) from a complex mixture of branched and cyclic alkanes, though the process is not complete.

The selective adsorption characteristics of zeolite molecular sieves have been used for the class separation of hydrocarbons and 5A sieves are now used in a standard technique for the unique partitioning of straight-chain alkanes, which are adducted, from branched and cyclic alkanes, which are not.

The 5A sieve is a crystalline calcium aluminosilicate containing "pores" 4.2Å in diameter, into which molecules with an effective diameter of up to 4.7Å may enter. Normal hydrocarbons with an effective cross-sectional diameter of 4.3Å penetrate the sieve and are retained, while the branched chain and cyclic hydrocarbons have a diameter >5Å and are excluded.

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*Present address: Geochemistry Unit, School of Chemistry, The University, Bristol, 8.

Successful extension of the sieving technique to permit the further subdivision of hydrocarbon mixtures would be of major importance in facilitating the examination of extracts. It was hoped that the recently available 7A mordenite sieve* with window cross-section intermediate between that of the 5A and the 10X type sieves would permit adduction of (methyl-) branched chain alkanes (critical molecular diameters _ca._ 6.1Å), but would exclude the more bulky cyclic compounds (with critical diameters $>$ 8Å).

The solvents normally used in 5A sieving i.e. benzene and iso-octane are no longer suitable as they have molecular diameters of about 5.9Å and 6.1Å respectively, and would be adducted by the 7A sieve. The use of solvents of larger molecular dimensions was examined. As anticipated mesitylene and 1,3,5-triethylbenzene gave inefficient separation due to their absorption into the sieve, while with tri-_n_-butylamine surface adsorption on cationic sites was the possible cause of poor separation.

1,3,5-Triisopropylbenzene* was chosen as solvent as its bulk (diameter $\sim$8.0Å) would prevent its entry into the sieve, and the complexing ability and reactivity of the aromatic ring would enable removal by either physical or chemical means. One disadvantage of this solvent is that it contains benzylic tertiary hydrogen atoms which are potential sites for radical attack and consequent decomposition, and some evidence of this was apparent in our experiments.

Experiments were first conducted using the 7A sieve in both pellet and powder form to separate standard mixtures of cholestane/squalane and cholestane/2-methyltricosane. It was possible to obtain 98% pure cholestane in 80-90% yield as the non-adduct from a cholestane/squalane mixture, either by heating a solution in triisopropylbenzene with the sieve in a sealed tube at 160° for 48 hr. or by the technique described below; substantially pure squalane was recovered from the adduct in less consistent yield. The optimum conditions derived for the most complete separation were then applied to the simplification of a branched/ cyclic hydrocarbon mixture from a geological source.

The organic extract from the Green River Shale (Eocene) was obtained by normal procedures (5), and the hydrocarbon fraction isolated by chromatography. Adduction of the n-alkanes in

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*The sieve was manufactured by the Davison Chemical Division of W. R. Grace Co., and was obtained through the courtesy of Dr. B.J. Mair, past director of the American Petroleum Institute's Project 6. It consists of 16-50 mesh beads containing 80% mordenite with 20% attagel for binding. Synthetic mordenite has the composition $Na_8(AlO_2)_8(SiO_2)_{40}24H_2O$, and has a pore diameter of 6.6Å (henceforth referred to as 7A sieve).

*Obtained from Rutgerswerke und Teerverwertung A.G. Castrop-Rauxel, W. Germany. The 1,3,5-triisopropylbenzene was re-distilled and stored over 5A molecular sieve.

a 5A sieve left the branched/cyclic fraction containing the usual preponderence of pristane, phytane, steranes, triterpanes and perhydrocarotane, (Fig. 1A).

The branched/cyclic fraction (27mg.) was dissolved in triisopropylbenzene (2.5ml.) and stirred with 7A mordenite **sieve*** **(1.2g)** in an atmosphere of nitrogen for 2 hr. The supernatant solution was pipetted off and the sieve was washed five times with further portions of triisopropylbenzene at $80-90^{\circ}$ for 30 min.

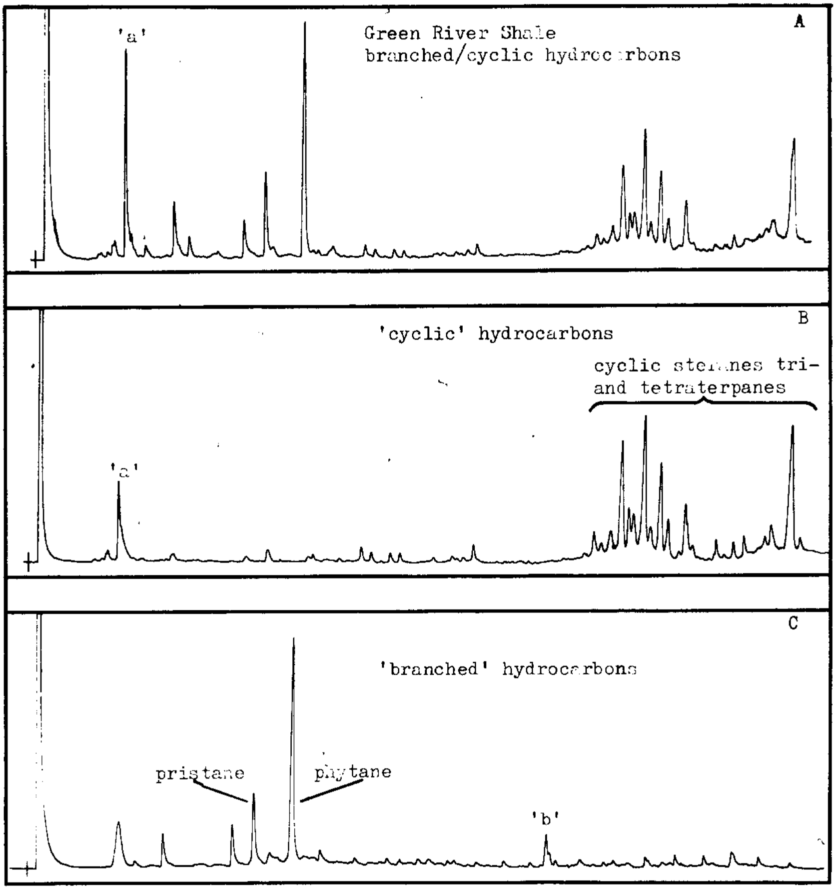

FIGURE 1. Gas liquid chromatograms of Green River Shale branched/cyclic alkanes. Conditions: column 20' x 1/16" containing 3% OV-1 on 100-120 mesh Gas Chrom Q, nitrogen 7.5ml/min., temperature programmed from $100-310^{\circ}$ at 2°/min. Peak marked 'a' is a contaminant in the original branched/cyclic mixture, that marked 'b' is a decomposition product of the solvent.

(a) Non-Adduct

Silica gel impregnated with 10% silver nitrate was prepared by dissolving $AgNO_3$ (2g) in a minimum of water, diluting with methanol (50ml) and adding silica gel (20g) with shaking. After

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*The sieve was activated prior to use by heating at 300° for 48 hr. under reduced pressure (0.5mm.Hg), and stored in a desiccator.

evaporation on a rotary evaporator at reduced pressure for 1 hr, the powder was activated for 1 hr. at 100°.

The combined washings were eluted, with n-hexane, from a column containing this impregnated silica gel. Triisopropylbenzene was strongly adsorbed on the column and the hexane eluate was evaporated to leave the saturated cyclic hydrocarbon fraction (10mg). Gas chromatography (Fig. 1B) shows the predominance of triterpanes in the non-adduct with almost complete absence of pristane, phytane, and other branched hydrocarbons.

(b) Adduct

The sieve was just covered with distilled water and an equal portion of hexane, and destroyed (taking the usual safety precautions) by addition of 40% hydrofluoric acid. Excess hydrofluoric acid was destroyed with a saturated boric acid solution and the organic layer was extracted with hexane. The solvent was evaporated and the residue passed down a column of silica gel impregnated with 10% silver nitrate as before, to remove residual traces of triisopropylbenzene. Evaporation of the eluate left a hydrocarbon fraction (2.5mg) which was shown by g.l.c. to consist almost entirely of the branched chain alkanes (Fig. 1C).

For larger scale work an alternative procedure was used for removal of the 1,3,5-triisopropylbenzene. This involved sulphonation of the aromatic ring by agitation of a hexane solution of the adduct (or non-adduct) and 1,3,5-triisopropylbenzene with oleum for 48 hr. The resulting sulphonic acid was then removed by aqueous washings and finally by elution through a short alumina column. An alternative sulphonation technique using chlorosulphonic acid gave neutral sulphonyl chlorides which proved difficult to remove.

Attempted separation by formation of a π complex between picric acid and triisopropylbenzene failed, presumably because of steric interactions. (Other π complexing reagents used for aromatic hydrocarbons, i.e. styphnic acid, 1,3,5-trinitrobenzene, 2,4,7-trinitrofluorenone etc. will not work for the same reason).

The identity of the major marked peaks has been confirmed by analysis on an LKB 9000 combined gas chromatograph - mass spectrometer (6,7).

An alternative procedure for separation of branched from cyclic hydrocarbons by selective adsorption on Sephadex LH 20 has been investigated. The complete resolution of a cholestane (2.8mg)/squalane (2.7mg) mixture has been achieved on a long column (95cm x 1.2cm) containing Sephadex LH 20. Acetone/tetrahydrofuran (1:1) was used as solvent and the elution was controlled at a very slow drop rate, fractions of 1.2ml being collected. The squalane was eluted first indicating that adsorption factors are more important than molecular dimensions in this case. Unexpected orders of elution from Sephadex have previously been reported by Mair et.al. (8) and the same order of elution found under a variety of conditions in a recent study (9) of retention times for steroids and their derivatives.

These results have also been confirmed independently by Dr. B.S. Cooper and will appear in a forthcoming publication together with an examination of a complex branched/cyclic hydrocarbon mixture under similar conditions. We will also report on the application of the 7A sieving technique as applied to complex hydrocarbon mixtures from two dissimilar geological sources.

Acknowledgement:- Thanks are due to Dr. B. J. Mair, for generously providing samples of the 7A sieve. We are indebted for financial support to N.E.R.C. (G.D.), British Petroleum (A.G.D.), N.A.S.A. (I.M. NsG101-61), and to S.R.C. for a grant (B/SR/2398; to Drs. C.J.W. Brooks and G. Eglinton), for purchase of the LKB 9000 gas chromatograph - mass spectrometer.

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