Table 1 *Slope of the straight lines drawn for temperatures and TRMs (for 7 hr and 2.5 hr cooling times) and the slope of the straight lines drawn for NRMs and TRMs (for 7 hr and 2.5 hr cooling times) for the samples obtained from excavated sites*

Excavated sites	Nature of the sample	Slope of the line × 10^6		Ratio of slopes	NRM/TRM	
		7 hr	2.5 hr		7 hr	2.5 hr
Kanchipuram	Pottery	1.10	0.51	2.16	1.095	2.237
Kanchipuram	Pottery	1.29	0.68	1.90	0.874	1.709
Kanchipuram	Amphorae	2.80	1.31	2.14	0.693	1.359
Kanchipuram	Brick	6.96	2.51	2.77	1.011	1.636
Vallam	Pottery	0.79	0.44	1.80	1.284	2.650
Vallam	Brick	6.00	1.55	3.87	1.284	2.800
Vallam	Tile	2.57	0.96	2.60	0.770	1.433
Uraiyur	Pottery	1.42	0.72	1.98	1.048	2.143
Uraiyur	Brick	5.20	1.95	2.66	0.922	1.850
Guttur	Tile	0.84	0.41	2.02	1.048	2.000
Guttur	Pottery	1.00	0.54	1.85	1.105	2.500

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1. Nagata, T., *Bull. Earthq. Res. Inst.*, 1943, **21**, 1.
2. Thellier, E. and Thellier, O., *Ann. Geophys.*, 1959, **15**, 285.
3. Dodson, M. H. and McClelland Brown, M. E., *J. Geophys. Res.*, 1980, **85**, 2625.
4. Fox, J. M. W. and Aitken, M. J., *Nature, (London)*, 1980, **283**, 462.
5. Halgedahl, S. L., Day, R. and Fuller, M. D., *J. Geophys. Res.*, 1980, **85**, 3690.
6. Gunn, N. M. and Murray, A. S., *Geophys. J. R. Astron. Soc.*, 1980, **62**, 345.
7. Blackett, P. M. S., *Philos. Trans. R. Soc.*, 1952, **A245**, 309.
8. Collinson, D. W., *Geophys. J. R. Astron. Soc.*, 1970, **19**, 547.
9. Tanguy, T. C., *Earth Planet. Sci. Lett.*, 1975, **27**, 314.

POLYNUCLEAR AROMATIC HYDROCARBONS (SYNTHESIS OF 6, 7, 13-TRIMETHYLBENZO [C] CHRYSENE THROUGH SPIRO-REARRANGEMENT)

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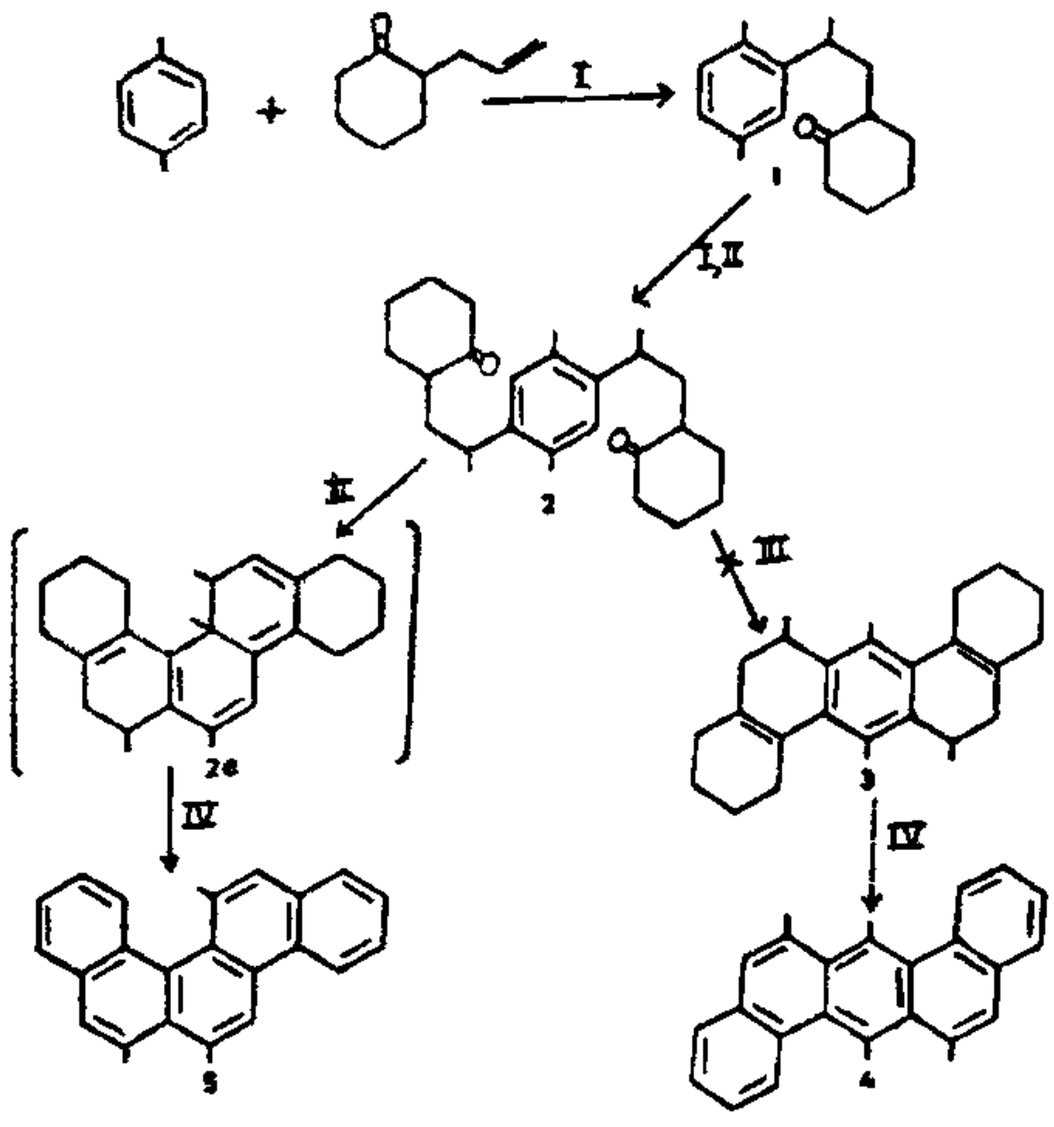
HARTWELL[1,2] reported that dibenz [a,h] -anthracene is carcinogenic and resembles benz [a] -anthracene in terms of structure. Newman[3] also reported synthesis of methyl substituted dibenz [a,h] -anthracenes as potential carcinogens. It was therefore considered worthwhile to synthesize 6, 7, 13, 14-tetramethyldibenz [a,h] -anthracene so that it might eventually prove a potential carcinogen.

2'-[β-(2, 5-Dimethylphenyl) propyl] cyclohexanone (1), obtained following the procedure of Mukherji and Bhattacharya[3], was subjected to cationoid alkylation with 2-allylcyclohexnone in the presence of anhydrous aluminium chloride in carbon disulphide solution to obtain *p*-bis-[β-(2'-oxocyclohexyl)-iso-propyl] -2, 6-dimethylbenzene in 32.8% yield. The diketone showed characteristic absorption at 1720 cm^{-1} in its IR spectrum (neat). The structure of the diketone (2) was further confirmed by its NMR spectrum exhibiting a 2H singlet at 6.83 δ assigned to two para protons, a 6H singlet at 2.20 δ for which the two methyl groups attached to the aromatic ring were found responsible. A 6H doublet at 1.14 δ was assigned to the two aliphatic

CHART-I



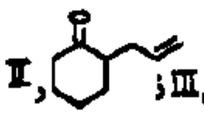
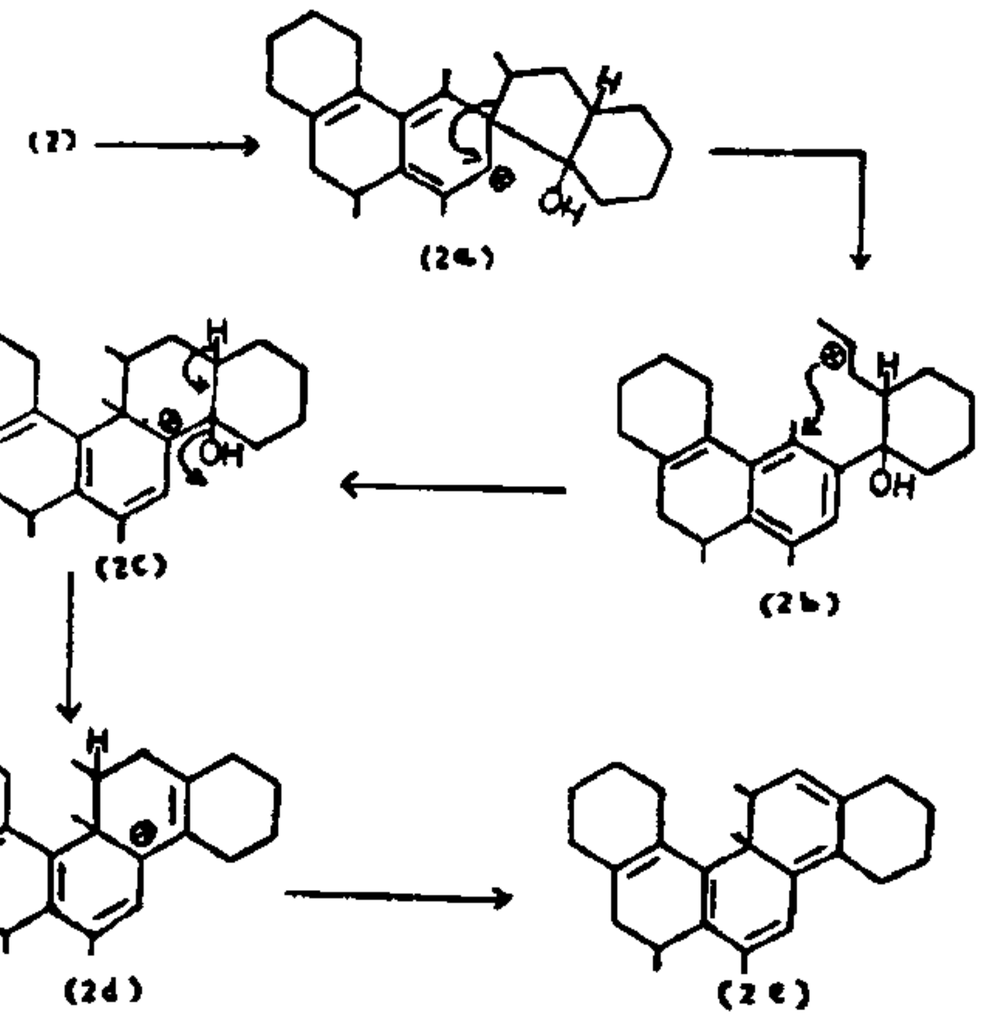
I, $AlCl_3$; II,  ; III, PPA ; IV, Pd/C 300-320/CO_2

CHART II

Mechanism of spirorearrangement



methyl groups and a 2H septet at 2.95 δ must be due to the two methylene protons, the other aliphatic protons resonating from 1.20 to 2.50 δ.

The diketone (2) was cyclized with PPA to provide a semisolid cyclodehydration product, the structure tentatively assigned as 6, 7, 13, 14-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13-dodecahydrodibenz [a,h] -athracene (3), subjected to dehydrogenation with 30% Pd/C at 320° in CO_2 atmosphere to procure a solid. The latter was converted into its picrate, and the benzene solution of the crystallized picrate was passed through a column of alumina and eluted with petroleum ether to obtain a 52.4% yield of pure (TLC) solid which melted at 72-73° and its picrate melted at 180-81°. It was tentatively assigned the structure (4). However, neither elemental nor NMR spectral analysis was compatible with the structure (4). Its 90 MHZ, NMR spectrum was a bit intriguing since it contained three 3H singlet at 2.55, 2.69 and 2.75 δ and an 11H aromatic pattern showing that the molecule contains three different kinds of methyl groups whereas the supposed 6, 7, 13, 14-tetramethyl-dibenz- [a,h] -anthracene (4) should have contained only two sets of 6H singlets with 10H aromatic region as the C-6, C-7, and C-7, C-14 methyl groups are symetrically situated. It was surprising that the presence of the three 3H singlets totally eliminated the proposed structure (4).

From the NMR spectrum, it was evident that the compound contained only three methyl groups and the C and H analysis further corroborated this fact. Thus, the aromatized product has been assigned the structure 6, 7, 13-trimethyl-benzo [c]- chrysene (5). The three methyl groups situated at entirely different chemical environment, should resonate at different magnetic fields in its NMR spectrum. The aromatic region contained a 2H multiplet from 7.75 to 9.95 δ which was assigned to H-12, H-14 protons and a 1H singlet at 8.43 δ which was assigned to H-5 proton. The H-1 and H-9 were located as a 2H multiplet from 8.05 to 8.25 δ. The proton H-14 and H-8 were broad singlet at 7.82 and 7.32 δ, whereas the multiplet from 7.80 to 7.60 δ was assigned to the remaining aromatic protons (i.e. H-10, H-11, H-2 and H-3). The methyl groups attached to 6, 7 and 13 positions gave rise to three 3H singlets at 2.55, 2.69 and 2.75 δ,respectively. The C-13 methyl group will obviously be expected to be most down field due to "bay interaction[5]". However, the assignments for the C-6 and C-7 methyl groups are based on the effect of ring currents on the chemical shifts.

The rationalization for the proposed structure may be provided by considering the report of Newman *et al*[6]. The cyclization of the two cyclohexanone rings is expected to take place (chart II) in two steps and probably after the first cyclization the

second cyclization ends up in the formation of a spirane structure (2a) and then the five-membered ring cleaves giving rise to another secondary carbonium ion (2b). The carbonium ion (2b) may then undergo intramolecular ipso-substitution[8,9] at the position of highest electron density to provide the ion (2c) which may undergo dehydration to given the ion (2d) and the latter may lose a proton to provide the structure (2e). Newman[9] reported formation of spirane during the process of cyclization. The formation of some anthraquinones have also been rationalized through spirocyclic rearrangement [6,10–12].

Experimental procedure:

The m.p. and bps are uncorrected. The IR spectra (λ_{max} in cm^{-1}) were recorded on a Beckman IR-20 and NMR spectra were run on Perkin-Elmer (R-32); tetramethyl silane was taken as internal reference and chemical shifts are expressed as displacements in ppm units (in δ scale) downfield from TMS.

p-Bis-[β-(2'-oxocyclohexyl) isopropyl] -2, 6-dimethyl benzene (2)

A solution of 2' -[β-(2, 5-dimethylphenyl) propyl] - cyclohexanone (1, 12.15g; 0.05 mole) in carbon disulphide (60 ml) was cooled in ice-salt bath. Anhydrous aluminium chloride (150 g; 0.112 mole) was added under protection from moisture in instalments of 1 g each followed by dropwise addition of 2-allylcylohexanone (II) (6.85; 0.05 mole) maintaining the temperature between 0 to 5° for 2 hr. After completion of the addition, stirring was continued for 1 hr at 0-5° and 4 hr at room temperature when the reaction mixture acquired brown colour. Thereafter the complex was poured into iced-hydrochloric acid and the organic phase separated, the aqueous phase was extracted with carbon disulphide (3 × 60 ml), the combined extract phase washed successively with dil. hydrochloric acid, water 5% $NaHCO_3$ and finally with water and dried ($mgSO_4$). On stripping off solvent and distillation in vacuo, b.p. 245-255°/6 mm, and column chromatography (silica gel/pet. ether 60-80/ benzene 1:1) was obtained 62 g (32.8%) of diketone (2) as viscous oil, IR (neat), 1720 ($\geq C = O$) NMR ($CDCl_3$) 6.83 (2H, s, p-aromatic protons); 2.25 (6H, s, two methyl groups); 1.14 (6H, d, two aliphatic methyl groups); 2.95 (2H, septet, methylene protons); 1.20 to 2.50 (other aliphatic protons), 2, 4-dinitrophenylhydrazone was prepared in the usual manner, m.p. 111-12°(Found: N, 14.9; $C_{38}H_{46}O_8N_8$ requires 15.10%).

6, 7, 13-Trimethylbenzo [c] chrysene (5):

The diketone (2; 20 g) was thoroughly mixed with PPA (8.0 g) (prepared from orthophosphoric acid 10 ml and phosphorus peroxide 18 g) and heated on a steam bath for 6 hr with stirring under protection from moisture. The reaction mixture was poured into crushed ice (500 g) and the organic layer was extracted with ether, washed successively with water, 5% aq. $NaHCO_3$, water and dried ($MgSO_4$). Removal of the solvent and column chromatoraphy over silica gel (elution with pet. ether 60–80°) provided 1.40 g (89.3%) of viscous oil which was directly used for the next step.

The hydroaromatic product (1 g) was dehydrogenated with 30% Pd/C (0.25 g) at 300–320° under CO_2 atmosphere for 4 hr. The reaction mixture was extracted with hot chloroform, the residue procured on removal of the solvent was converted into its picrate and recrystallized from slovent ether. The brick red-coloured picrate was dissolved in benzene and passed through a column of silica gel and eluted with pet. ether (60–80°).

Removal of the solvent provided a semisolid, which on crystallization from dilute ethyl alcohol afforded 0.54 g (52.4%) of white crystals, m.p. 71–72° (Found: C, 93.4; H, 6.1, $C_{25}H_{20}$ requires C, 93.75; H, 6.25%) IR (KBr) 1605 (ring breathing).

Picrate crystallized from solvent ether m.p. 181–82° (Found N, 7.6, $C_{31}H_{23}N_3O_7$ requires N, 7.65%).

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1. Fieser, L. R. and Hartwell, J. L., *J. Am. Chem. Soc.*, 1938, **60**, 2555 and references cited therein.
2. Hartwell, J. L., Survey of the compounds which have been tested for carcinogenic activity, U. S. Public Health Publication No. 149, U. S. Govt. Printing Office, Washington Dec., 1951.
3. Newman, M. S. and Blum, O. S., *J. Med. Chem.*, 1964, **7**, 466.
4. Bhattacharya, N. K. and Mukherji, M. S., *J. Org. Chem.*, 1952, **17**, 1202.
5. Bortle, K. D., Heaney, H., Joner, H. W., Leas, P., *Spectro. Chem. Acta*, 1966, **22**, 941.
6. Newman, M. S., Ohio State University Columbus, Ohio, 43210, Private Communication, 1967.
7. Taylor, R., *J. Chem. Soc.*, Perkin Trans., 1975, **2**, 277.

8. Taylor, A specialistic periodical report on Aromatic and heteroaromatic chemistry Chem. Soc., London, 1972–73, p. 242.
9. Newman, M. S., *Acc. Chem. Res..*, 1972, **5**, 354.
10. Noyee, D. S. and Kittle, P. A., *J. Org. Chem.*, 1965, **30**, 1899.
11. Hoyashi, M., *J. Chem. Soc.*, 1927, 2516, 1930, 1513, 1520, 1524.
12. Newman, M. S. and Ihrman, K. S., *J. Am. Chem. Soc.*, 1958, **80**, 3652.

EFFECT OF FEEDING *TRIGONELLA FOENUM GRACECUM* (METHI) LEAVES ON SERUM CHOLESTEROL, TRIGLYCERIDES AND HIGH DENSITY LIPOPROTEIN CHOLESTEROL IN THE NORMAL RABBITS

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THE seeds and leaves of *Trigonella foenum gracecum* (Methi) are reported to have carminative, anthelmintic, antipyretic, suppurrative, diuretic, aphrodisiac and emmenagogue properties useful for treatment of dropsy, chronic cough, enlargement of spleen, liver and heart diseases[1]. The seeds of fenugreek are reported to have hypocholesterolemic activity[1–5].

The aim of the present study is to find out the effect of oral administration of the green leaves of methi on serum lipids in normal albino rabbits, whose correlation with cardiovascular system is well established[6,7].

Fresh green leaves of 'methi' bought daily from the local market, were washed and cooked in steam. Sixteen normal adult male albino rabbits were maintained on Hindustan Gold Mohr rabbit feed for a month. After this period, serum lipids were estimated twice to check constancy of their levels, which was followed by feeding of experimental diet containing 10 g cooked green leaves along with basal diet *ad libitum* for eight weeks to the experimental group animals, consisting of eight rabbits, whereas the other group of remaining eight rabbits was kept on only control diet throughout. The animals had free access to food and water, however, their daily food consumption was between 95 and 100 g. Fasting blood samples were drawn at the end of first week, second week, fourth week and eighth week,

Table 1 *Effect of feeding Trigonella foenum gracecum green leaves (10 g/day) in cooked form for eight weeks on serum total cholesterol, triglyceride (TG) and high density lipoprotein (HDL) cholesterol in normal rabbits. (Values are mean ± SD, expressed in mg/day)*

		Experimental group+			
	Control group+	Ist Wk	2nd Wk	3rd Wk	4th Wk
Body weight (in kg)	1.5150 ±0.127	1.5340 ±0.120** (1.25)	1.5540 ±0.117** (2.57)	1.5760 ±0.104* (4.03)	1.6220 ±0.136 (7.06)
Cholesterol	102.01 ±9.07	96.15 ±8.73*** (5.74)	91.12 ±10.87** (10.68)	85.57 ±12.60** (16.12)	79.27 ±9.62* (22.29)
Triglycerides	202.03 ±9.04	187.14 ±14.64** (7.37)	149.47 ±23.21* (26.02)	137.95 ±15.06* (31.72)	123.39 ±14.16* (38.92)
HDL–Cholesterol	37.15 ±4.24	40.70** ±4.12 (9.56)	46.12 ±4.66* (24.15)	49.84 ±3.67* (34.16)	51.67 ±3.55* (39.08)

+ Sample size in each case was 8. Figures in parentheses indicate per cent change. *$P < 0.001$; **$P < 0.01$; ***$P < 0.05$.