Table 1 *Topological distances of oxy-alcohols*

Compound	W	$\overline{W}$	W_{rms}
Methyl alcohol	0.34	0.34	0.34
Ehyl alcohol	2.68	0.9933	0.9850
n-Propyl alcohol	8.02	1.3366	1.4936
Iso-propyl alcohol	7.02	1.1700	1.2719
n-Butyl alcohol	17.36	1.7360	1.9632
Iso-butyl alcohol	15.36	1.5360	1.6692
Sec-butyl alcohol	15.36	1.5360	1.7082
t-Butyl alcohol	13.36	1.3360	1.4318
n-Amyl alcohol	31.70	2.1133	2.4135
t-Amyl alcohol	24.70	1.6466	1.8069
Iso-amyl alcohol	28.70	1.9133	2.1244
Neo-pentyl alcohol	24.70	1.6466	1.7576
1-Hexanol	52.04	2.4780	2.8526
1-Heptanol	79.38	2.8350	3.2846
1-Octanol	114.78	3.1866	3.7117
1-Decanol	159.06	3.5346	4.1352

Table 2 *Correlation equations for normal oxy-organic compounds boiling points vs* W_{rms}

Compounds	Boiling point (°C)	Standard deviation
Alcohols	$40\ W_{rms} + 36$	2.803
Ethers	$60\ W_{rms} - 48$	1.776
Aldehydes	$65\ W_{rms} - 70$	0.2636
Ketones	$55\ W_{rms} - 26$	1.757
Carboxylic acids (mono)	$48\ W_{rms} + 58$	1.343

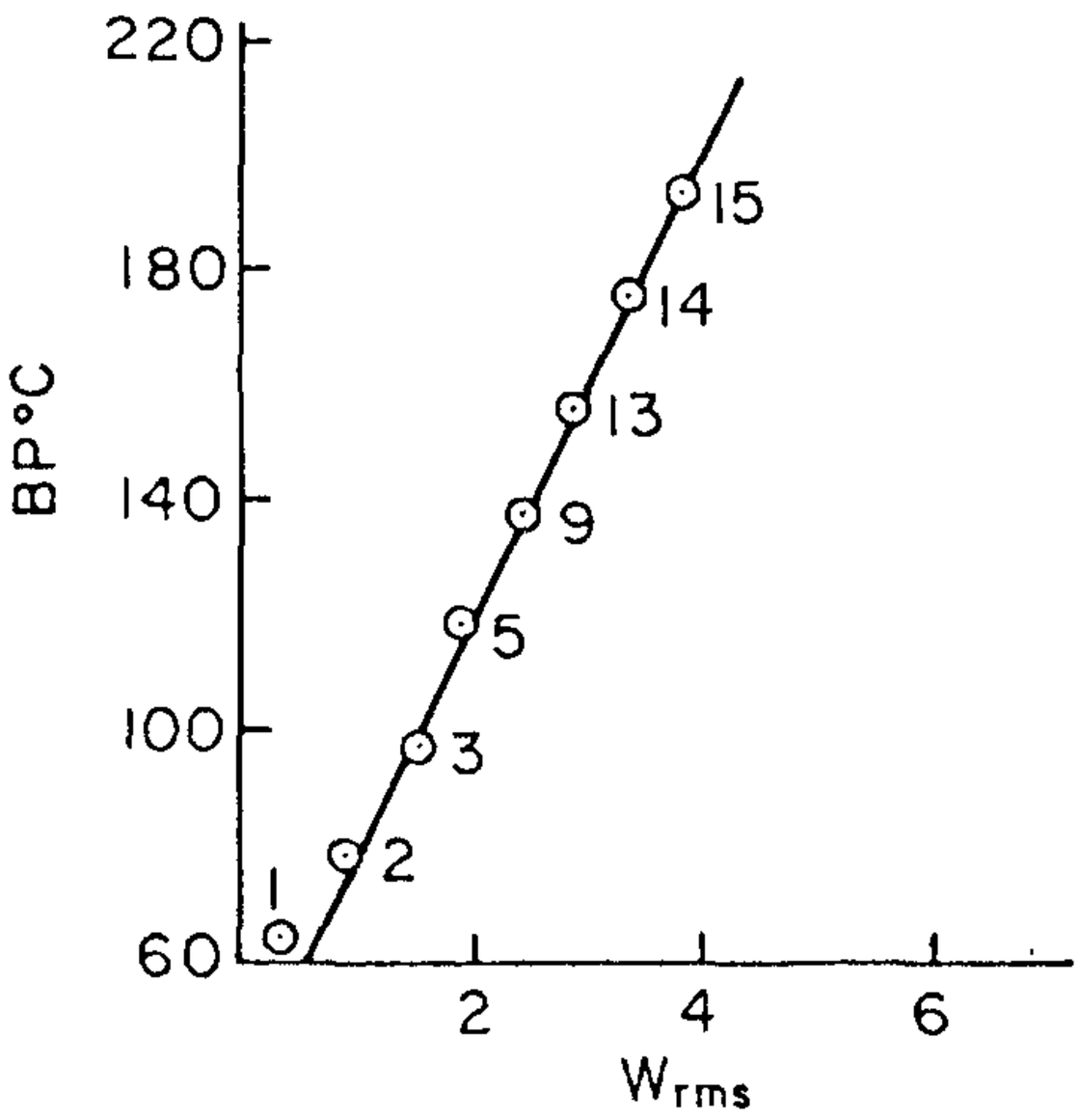

Figure 1. Variation of boiling points of normal oxy-alcohols with topological index W_{rms} (data of experimental BP from ref. 13)

branched alkyl groups. The correlation of the physical properties with the number of carbon atoms and the molecular formula weight has been reported by some authors[10, 11]. The topological studies of the compounds in a homologous series are much more interesting, as the topological index provides a fundamental basis for all types of compounds. The topological studies from edge-weighted graphs are more applicable in biological compounds[6, 12].

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FURTHER EVIDENCE TO THE STRUCTURE OF SEMECARPUFLAVANONE*

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FROM the defatted nut shells of *Semecarpus anacardium* Linn., two new compounds[1, 2] jeediflavanone(IV) and semecarpuflavanone(V) besides the three known biflavanones[3] A(I), B(II) and C(III) have been recently

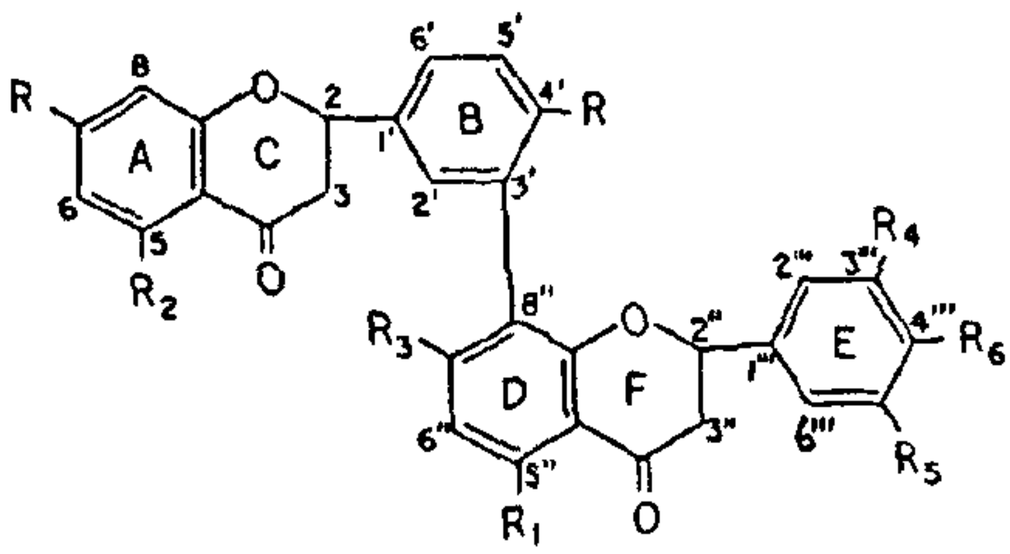
*Part IV in the series partial conversions in biflavonoids for Part III see ref 6.

isolated. The structures for the first three compounds (I–III) were confirmed earlier[4–6]. The present study further supports the structure of semecarpuflavanone(V).

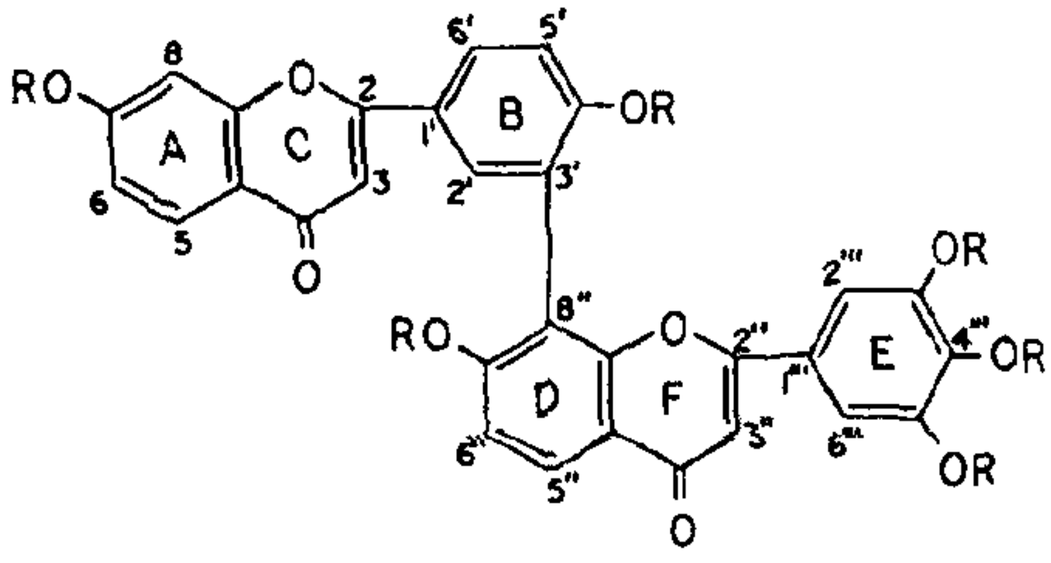
Semecarpuflavanone(V) was dehydrogenated[7,8] by refluxing with iodine and potassium acetate in glacial acetic acid for 3 hr to furnish the corresponding, relatively more stable biflavone which has been designated as SA4. It appeared as a light yellow powder from acetone, $C_{30}H_{18}O_{10}$, m.p. $>300°$, UV(EtOH): nm, 255, 302, 378; + NaOAc, 256, 327, 431; + $AlCl_3$, 255, 301, 379; IRν(Nujol) 3530–3290 (broad, OH), 3170 (OH), 1685 and 1680 (flavone carbonyls), 1600 and 1585 (aromatic) cm^{-1}. Preliminary characterization showed that it is a polyhydroxybiflavone.

The PMR spectrum of SA4 in acetone-d_6 showed a singlet signal* due to one C-3 and one F-3″ protons at 3.48. The three protons at 6′, 2′ and 5′positions of ring B appeared respectively at 2.28 (q, 1H, J = 2, 8 Hz), 2.43 (d, 1H, J = 2 Hz) and 2.84 (d, 1H, J = 8 Hz). The two signals at 2.9 (d, J = 2 Hz) and 2.98 (d, J = 2 Hz) each integrating for one proton corresponded to the two meta-coupled protons at 2‴ and 6‴ positions of ring E. The three protons corresponding to 5, 6 and 8 positions of ring A could readily be noticed at 3.62 (d, J = 8 Hz), 3.9 (dd, J = 2,8 Hz) and 3.74 (d, J = 2 Hz) respectively. No low field proton could be observed in its PMR spectrum indicating the absence of chelated hydroxyl groups in SA4. But six non-chelated D_2O exchangeable hydroxylic protons are noticed at 1.54 (s, 1H), 2.14 (s, 2H) and 2.39 (s, 3H) and these could be ascribed to A-7, B-4′, D-7″ and E-3‴, 4‴, 5‴ positions. There are two more doublets at 3.14 (1H, J = 8.5 Hz) and 3.34 (1H, J = 8.5 Hz) corresponding to the two ortho-coupled protons at 5″ and 6″ positions of ring D respectively.

On methylation with dimethyl sulphate and potassium carbonate, SA4 furnished a hexamethyl ether(VII), $C_{36}H_{30}O_{10}$, m.p. 190–91° whose PMR spectrum in $CDCl_3$ showed signals due to six methoxyl groups at 6.22 (s, 2 × 3H) and 6.30 (s, 4 × 3H). Further, oxidation of SA4 hexamethyl ether(VII) with neutral permanganate afforded only one mole of gallic acid trimethyl ether suggesting that one of the side-phenyls is involved in the diaryl linkage. With the foregoing evidence, structure(VI) has been assigned for compound SA4. Mass spectral fragmentation pattern of SA4 methyl ether also supports this assignment (scheme 1).



I R = R_1 = R_2 = R_4 = R_6 = OH, R_3 = R_5 = H
II R = R_1 = R_2 = R_3 = R_6 = OH, R_4 = R_5 = H
III R = R_3 = R_6 = OH, R_1 = R_2 = R_4 = R_5 = H
IV R = R_1 = R_2 = R_3 = R_4 = R_6 = OH, R_5 = H
V R = R_3 = R_4 = R_5 = R_6 = OH, R_1 = R_2 = H

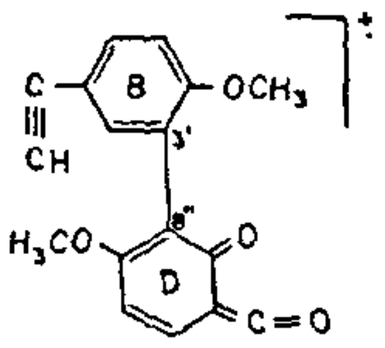


VI R = H
VII R = CH_3

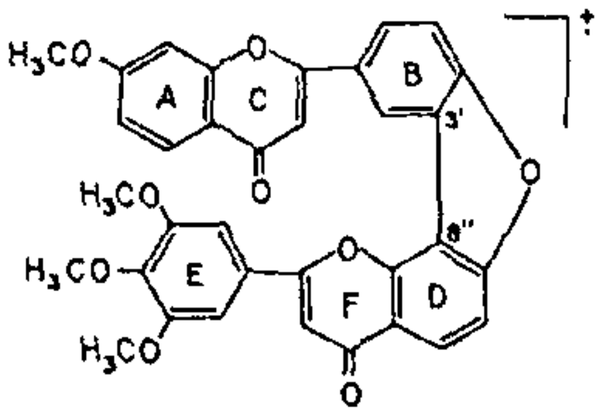
Scheme 1

SA4 hexamethyl ether(VII) showed the molecular ion M^+ at m/e 622. It furnished two ions at m/e 192 [3,4,5-$(H_3CO)_3.C_6H_2.C{\equiv}CH]^+$ and m/e 195 [3,4,5-$(H_3CO)_3.C_6H_2.C{\equiv}O^+$] suggesting that rings E and F are not involved in the biflavonoid linkage. The peak at m/e 280 corresponding to the central fragment(VIII) is formed after two RDA fragmentations. SA4 methyl ether showed a peak at m/e 576 which is formed by the loss of 46 mass units. This fragment can be formulated as IX in which the ortho-methoxyl groups to the biphenyl linkage cyclise to a furan ring. Perhaps the most significant feature is the formation of the two fragments (VIII) and (IX) which clearly revealed that the C–C linkage is between rings B and D. Overall, the mass spectral fragmentation exhibits a close similarity to that of amentoflavone hexamethyl ether[9]. The peaks at m/e 607, 592 and 577 arise due to the loss of 15 mass

* Chemical shifts throughout the article in τ scale.



VIII



IX

Scheme 2

units while the peaks at m/e 591 and 560 obtained due to the loss of 31 mass units (scheme 2).

From the foregoing spectral and chemical evidences, the assignment of structure(VI) for the biflavone SA4 is taken as supporting evidence for the structure of semecarpuflavanone(V).

The author is grateful to Professor L. R. Row for encouragement. His thanks are also due to Dr P. A. Ramaiah for the PMR and mass spectra recorded.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF THORIUM (IV)

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MOST of the proposed methods for the spectrophotometric determination of thorium (IV) suffer from disadvantages like extraction, low sensitivity[1] or allowing the solution to stand for a long time for maximum colour development[2]. Sodium 5-(4-diethyl-amino-2-*hydroxy phenylazo)* 1,2,4-*triazole*-3-carboxylate (SATC) was synthesised[3] and proposed for the spectrophotometric determination of cobalt present in natural and geological materials[4] and in uranium (VI)[5]. The present investigation deals with the study of the colour reaction of SATC with thorium (IV) for the rapid spectrophotometric determination of traces of thorium.

A stock solution of thorium (IV) was prepared from AR grade thorium (IV) nitrate and standardised[6]. A 0.02% solution of SATC was prepared in doubly-distilled water. Walpole buffer solutions[7] of pH values from 3.72–5.80 were prepared by mixing 0.2 N acetic acid and 0.2 N sodium acetate solutions. The absorbance was measured with a spectrophotometer (Beckman model DB).

An aliquot of the stock solution containing 1.5–142.5 *μg of thorium, 5 ml of a buffer (pH 4.27) and* 6 ml of 0.02% SATC solution was made up to 25 ml in a volumetric flask and its absorbance was measured at 535 nm against a corresponding reagent blank. The thorium (IV) content in the sample solution was then deduced from the standard calibration curve.

SATC reacts with thorium (IV) instantaneously to form a *reddish pink complex at room temperature* (27°C) in hydrochloric, sulphuric, phosphoric or acetic acid or acetic acid-sodium acetate buffer medium. The study of the Th (IV)-SATC complex in hydrochloric, sulphuric, phosphoric or acetic acid medium is not recommended because of lower stability (< 2 min), least sensitivity and interference of foreign ions at low *concentrations. Acetic acid-sodium acetate buffer* medium was therefore selected for further studies because of the greater stability of the complex and higher tolerance limits of the diverse ions in this medium. The effective pH range is 3.75 - 5.1. A buffer of pH 4.5 was therefore selected. A 3-fold molar excess of the reagent over thorium (IV) was necessary for full