

LETTERS TO THE EDITOR

ANOMALOUS THERMAL EXPANSION
OF FERROUS FLUORIDE

IN a recent publication¹ from this laboratory, while describing the results on the thermal expansion of cobalt fluoride (CoF_2), it has been mentioned that the behaviour of CoF_2 is peculiar in having the value of the coefficient of thermal expansion perpendicular to the c -axis (α_{\perp}) greater than the coefficient along the c -axis (α_{\parallel}), unlike other rutile type compounds for which α_{\parallel} is greater than α_{\perp} . Hence it is thought worthwhile to study the thermal behaviour of ferrous fluoride (FeF_2), a similar compound. The present communication gives the results on the thermal expansion of FeF_2 .

The sample used in this study has been obtained from Prof. Stout of the University of Chicago. Sharp powder lines with Bragg angles ranging from 61° to 83° , obtained with a Unicam 19 cm. high temperature powder camera and iron radiation from Raymax-60 X-ray unit, have been used for evaluating the lattice parameters. The experimental technique employed is the same as that described in an earlier paper.² The lattice parameters, obtained at different temperatures in the range 25°C . to 450°C ., are given in Table I and shown

TABLE I
Lattice parameters of FeF_2 at different temperatures

Temp. $^\circ\text{C}$.	a (\AA)	c (\AA)
28	4.6945	3.3097
87	4.7009	3.3091
161	4.7060	3.3083
210	4.7113	3.3068
258	4.7173	3.3054
306	4.7221	3.3040
354	4.7289	3.3024
401	4.7344	3.3011
449	4.7397	3.3001

TABLE II
 α_{\parallel} and α_{\perp} of FeF_2 at different temperatures

Temp. $^\circ\text{C}$.	$\alpha_{\parallel} \times 10^6$	$\alpha_{\perp} \times 10^6$
50	-1.51	17.57
90	-3.25	18.64
130	-4.98	19.86
170	-6.57	20.98
210	-7.86	22.05
250	-8.84	23.70
290	-9.29	24.87
330	-9.82	26.09
370	-10.05	27.53
410	-10.35	27.96

graphically in Figs. 1 and 2. The coefficients of thermal expansion at different temperatures are given in Table II.

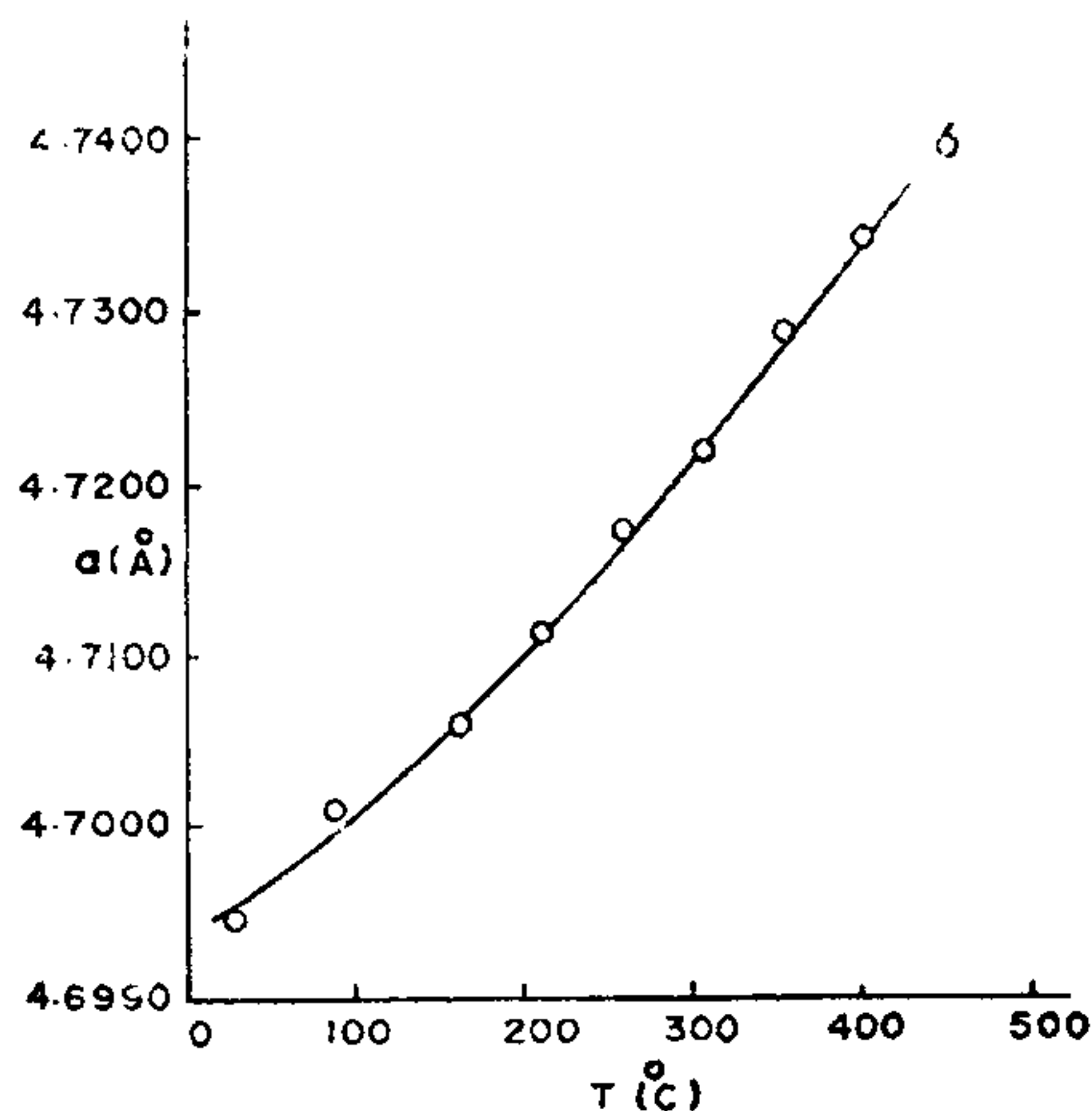


FIG. 1. Variation of a with temperature.

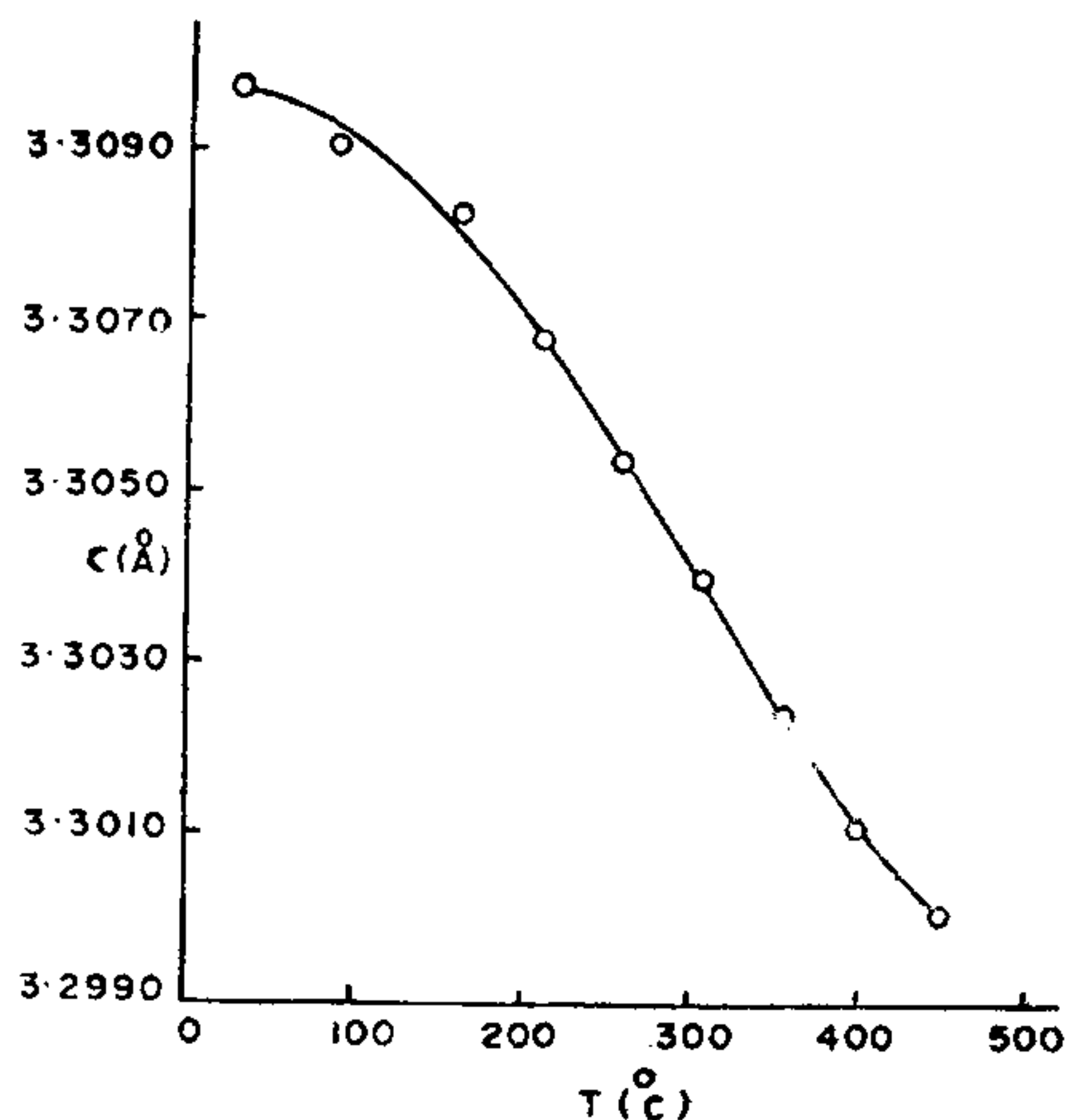


FIG. 2. Variation of c with temperature

It may be mentioned that the behaviour of FeF_2 is very abnormal in having a large value for α_{\perp} and negative value for α_{\parallel} . Recently Haefner³ studied the thermal expansion of FeF_2 from 10°K to 290°K and found that α_{\parallel} is positive throughout this range, whereas α_{\perp} is

negative between 10° K and 80° K and positive from 80° K to room temperature. Another rutile type compound having a negative α_1 is chromium dioxide (CrO₂).⁴ A detailed paper correlating the coefficients of thermal expansion with the other physical properties of rutile type compounds including FeF₂ will be published elsewhere.

In conclusion, the authors wish to thank the C.S.I.R., New Delhi, for sponsoring a Research Scheme, of which this investigation forms a part.

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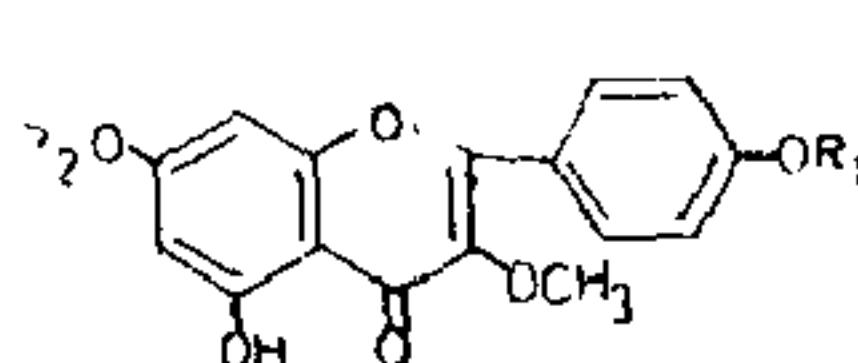
SYNTHESIS OF 3,7-*o*-DIMETHYL KAEMPFEROL AND 3,7,8-*o*-TRIMETHYL HERBACETIN

In connection with the study of the constitution of glycosides, several partial methyl ethers of flavonols have been needed. Many of these also occur free in nature. As part of this programme, we have now synthesised the compounds mentioned in the title, which have been found to be the components of a *Beyeria* species and *Ricinocarpus stylosus* respectively by Jefferies *et al.*^{1,2} The structures were assigned on the basis of methylation studies and alkali fission. Further support was provided by U.V. and N.M.R. studies. No synthetic confirmation has been provided. Like calycopterin occurring in the anthelmintic drug *Calycopteris floribunda*, they have the 5 and 4'-hydroxyls free.

The synthesis of *o*-dimethyl kaempferol (I) starts from *o*-methoxy phloracetophenone which was subjected to Allan-Robinson condensation with the anhydride and the sodium salt of *p*-benzyloxy benzoic acid. The flavonol (III)³ thus obtained was partially methylated in the 7-position. The resulting methyl ether (IV), m.p. 131–32°, was subjected to catalytic debenzoylation to get the desired flavonol (I), m.p. 252–53° (lit.¹ 253–54°); mixed m.p. with natural sample was undepressed; UV spectra were identical.

o-Trimethyl herbacetin (II) has been synthesised starting from 2, 4-dihydroxy-*o*-3, 6-trimethoxy acetophenone⁴ which was subjected to Allan-Robinson condensation with the

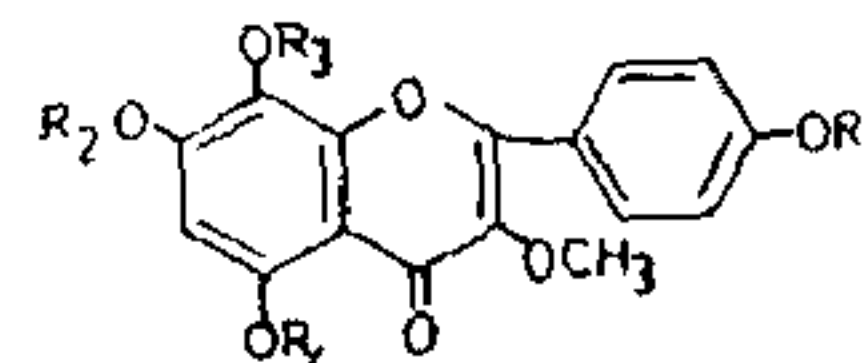
anhydride and the sodium salt of *p*-benzyloxy benzoic acid. The flavonol (V) thus obtained, m.p. 247–49°, was fully methylated and the resulting methyl ether (VI), m.p. 134–35°, was subjected to catalytic debenzoylation. The resulting tetramethyl ether (VII), m.p. 262–63°, was partially demethylated using aluminium chloride in acetonitrile to give the desired flavonol (II), m.p. 267–68° (lit.² 266–68°); mixed m.p. with natural sample was undepressed and UV spectra were identical.



I, R₁ = H; R₂ = CH₃

III, R₁ = C₇H₇; R₂ = H

IV, R₁ = C₇H₇; R₂ = CH₃



II, R₁ = R₂ = H, R₃ = CH₃

V, R₁ = C₇H₇; R₂ = H; R₃ = R₄ = CH₃

VI, R₁ = C₇H₇; R₂ = R₃ = R₄ = CH₃

VII, R₁ = H; R₂ = R₃ = R₄ = CH₃

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CHEMICAL INVESTIGATION OF ROOT- BARK AND STEM-BARK OF *ALANGIUM* *LAMARCKII* THWAITES

In our previous communications we have reported¹ the isolation of two alkaloids from the fruits of *Alangium lamarkii* which were identified as N-methyl cephaeline and deoxy-tubulosine.² Although the root-bark and the stem-bark of the above plant have been investigated by other workers,³ we were unable to get any alkaloids reported by them, from the material we had at our disposal. Both the root bark and stem-bark were found by us to contain the same alkaloids as indicated by thin layer chromatogram (R_f values, 0.12, 0.19, 0.31 and 0.4) using a chloroform-methanol (15%) system. From the alkaloid mixture only one alkaloid could be isolated in a pure crystalline condition by chromatography over alumina. The portion eluted with benzene-ether (1:3) crystallised from dilute methanol in colourless needles, m.p. 256–57°.