

TABLE 2—¹³C CHEMICAL SHIFT DATA FOR 2-PHENYL-CYCLOHEX-2-EN-1-ONE (2) AND 2-ARYL-2-CYCLOHEXEN-1-ONE OXIMES (1a-c)

Compd.	Chemical shift in ppm									
	O ₁	O ₂	O ₃	O ₄	O ₅	O ₆	O _{1'}	O _{2',6'}	O _{3',5'}	O _{4'}
2-Phenyl-cyclohex-2-en-1-one (2)	197.8	140.3	147.9	26.9	22.9	39.0	186.5	128.6	127.9	127.5
2-Phenyl-cyclohex-2-en-1-one oxime (1a)	155.9	139.2	135.6	22.6	20.9	25.5	186.9	128.9	127.9	127.0
2-(4-Methylphenyl)-cyclohex-2-en-1-one oxime (1b) ^a	156.1	136.6	135.3	22.6	20.9	25.5	186.3	128.7	128.6	135.3
2-(4-Isopropylphenyl)-cyclohex-2-en-1-one oxime (1c) ^b	155.8	136.6	134.8	22.3	20.7	25.2	186.4	128.6	125.7	147.3

^aAr—CH₃ appears at δ 21.1.^bOther signals present are at δ 23.8 (CH₃) and 33.6 (OH).

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Biflavones from *Thuja javanica* and *Thuja gigantea*

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THE genus *Thuja* (Cupressaceae) consists of several species of evergreen trees and shrubs. Sawada¹ in his studies on the distribution of biflavonoids

reported the presence of hinokiflavone in *Thuja standishii* and *T. occidentalis*. Besides these two, four more species have been analysed for their flavonoidic constituents. The present paper deals with the isolation and characterisation of amentoflavone, I-7-mono-*O*-methylamentoflavone, hinokiflavone, I-7, II-7-di-*O*-methylamentoflavone, I-7, I-4', II-4'-tri-*O*-methylamentoflavone from *Thuja javanica* and *T. gigantea*. The structure of these compounds were confirmed by their spectral data and by comparison with authentic samples.

T. javanica and *T. gigantea* were collected from Government Botanic Gardens, Ooty (India). The dried and crushed leaves of *T. javanica* were extracted with boiling acetone. The combined acetone extracts were concentrated under reduced pressure. The dark green gummy mass so obtained was refluxed with petroleum ether (b.p. 60–80°), benzene, chloroform, ethyl acetate and acetone till the solvent in each case was almost colourless. The ethyl acetate fractions were mixed together and dried under reduced pressure. It was then purified on silica gel column, eluting successively with petroleum ether, benzene, benzene-ethyl acetate (90 : 10, 85 : 15), and ethyl acetate. The last three fractions gave usual flavonoid colour test, which were combined and separated into five components by preparative tlc (benzene-petroleum ether-acetone, 36 : 9 : 5) and labelled as TI to TV in order of increasing R_f values.

TI on methylation and acetylation and comparison with authentic samples² was found to be hexaacetate and hexamethyl ether of amentoflavone. The compound TII on acetylation gave a pentaacetate and confirmed as I-7-*O*-methyl ether of amentoflavone (sequoiaflavone) by comparing its spectral data with those of the authentic specimens. The compound TIII, m.p. 345°, gave a pentaacetate, m.p. 240° and methyl ether, m.p. 260°. It was characterised as hinokiflavone by nmr studies. TIV gave a tetraacetate and a methyl ether, the structure was finally established as I-7, II-7-di-*O*-methyl ether of amentoflavone⁴. TV was

confirmed as I-5, II-5, II-7-trihydroxy-I-7, I-4', II-4'-tri-*O*-methyl [I-3', II-8]biflavone by comparison of ^1H nmr data of its acetate and methyl ether with those of the authentic samples.

The dried and powdered leaves of *T. gigantea* on similar treatment led to the isolation and characterisation of the same biflavones, viz. amentoflavone, I-7-mono-*O*-methylamentoflavone, hinokiflavone, I-7, II-7-di-*O*-methylamentoflavone, I-7, I-4', II-4'-tri-*O*-methylamentoflavone. These compounds were identified by m.p., m.m.p., R_f , characteristic fluorescence in uv light, ^1H nmr and finally by comparison with reference samples.

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Amperometric Determination of Trace Amounts of Gallium(III), Indium(III) and Thallium(I) using Xylenol Orange

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IN continuation of the previous work¹⁻³ on the amperometric determination of trace amounts of rare earths and some transition elements using xylenol orange, the present paper deals with the use of the same reagent for the trace determination of Ga^{III} , In^{III} and Tl^{I} . The titration procedure has been supplemented by spectral studies.

Experimental

All the chemicals were of AnalaR grade. Solutions of Ga^{III} , In^{III} and Tl^{I} were prepared by dissolving metal nitrates in double-distilled water and standardised⁴. The solution of xylenol orange was prepared by dissolving a requisite quantity of the reagent in double-distilled water. Amperometric titrations were performed on a manually operated polarograph with a multiflex galvanometer (sensitivity 8.1×10^{-9} A/div) used to measure the current. A d.m.e. and a saturated calomel electrode were used as an indicator and reference electrode, respectively. The capillary used for the d.m.e. had a m value of 2.373 3 mgs^{-1} , at a drop time of 3.0 s in air-free 1M KCl at 41 cm effective height of mercury column ($m^{2/3} t^{1/3} = 2.316 \text{ mg}^{2/3} \text{ s}^{-1/3}$). The amperometric titrations were performed at $70 \pm 1^\circ$, maintained on a thermostat. Below this temperature the polarogram of xylenol orange was not well defined and the diffusion current was not proportional to the xylenol orange concentration. A Elico LI-120 digital pH meter was used to measure pH.

Voltammogram of xylenol orange: Xylenol orange gave a well defined two-step reduction wave⁵ in 0.3 M KCl, $\text{pH} = 4.0 \pm 0.02$, $\mu = 0.3$ and at $70 \pm 1^\circ$. The polarograms of xylenol orange at its different concentrations were recorded and it was observed that the diffusion current for the second wave is proportional to its concentration. The plateau potential for the second step is at -1.10 V vs S.C.E.

Procedure for amperometric titrations: Solutions containing known amounts of xylenol orange in 0.3 M KCl as supporting electrolyte were prepared and pH of the solutions was adjusted to 4.0 ± 0.02 using acetate buffer. The temperature of each set was maintained at $70 \pm 1^\circ$ in a thermostat during the course of pH measurements and amperometric titrations. The plateau potential, -1.10 V vs S.C.E., was fixed on a potentiometer. Standard solution of the metal ions were added dropwise from a semimicro burette. The current was noted on a multiflex galvanometer.

TABLE 1—AMPEROMETRIC DETERMINATION OF Ga^{III} , In^{III} AND Tl^{I} WITH XYLENOL ORANGE

Plateau potential = -1.10 V vs S.C.E., $\mu = 0.3$ (KCl), $\text{pH} = 4.0 \pm 0.02$, Temp. = $70 \pm 1^\circ$

Concn. $\times 10^4$	Ga^{III} (mg) Taken/ (Found)	% Error	In^{III} (mg) Taken/ (Found)	% Error	Tl^{I} (mg) Taken/ (Found)	% Error
1.0	0.0697 (0.0696)	-0.15	0.1148 (0.1140)	-0.73	0.2043 (0.2058)	+0.73
2.5	0.1742 (0.1754)	+0.68	0.2870 (0.2882)	+0.41	0.5107 (0.5119)	+0.23
5.0	0.3485 (0.3440)	-1.29	0.5440 (0.5470)	+0.55	1.0215 (1.0180)	-0.34
7.5	0.5127 (0.5139)	+0.23	0.8610 (0.8638)	+0.32	1.5311 (1.5350)	+0.25
10.0	0.6972 (0.6951)	-0.31	1.1480 (1.1468)	-0.10	2.0437 (2.0390)	-0.23
15.0	1.0457 (1.0478)	+0.20	1.7220 (1.7243)	+0.13	3.0652 (3.0601)	-0.16