

All these thirty angular and linear  $\alpha$ -pyronochromones and the other eight linear  $\alpha$ -pyronoiso-flavones previously described by us<sup>1</sup> were tested against three types of bacteria, viz., *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* by the tube dilution method<sup>7</sup>. In general a methyl group either in  $\alpha$ - or  $\beta$ -position of the  $\alpha$ -pyrone ring has been found to decrease the activity. Among fifteen 7,6- $\alpha$ -pyronochromones, 7,6- $\alpha$ -pyrono- $\beta$ ,3-dimethyl-2-(3',4'-dimethoxy) phenyl,  $\beta$ ,3-dimethyl-2-(3',4'-methylenedioxy) phenyl,  $\beta$ ,3-dimethyl-2-(4'-nitro) phenyl,  $\beta$ -methyl-3-phenyl,  $\beta$ -methyl-2-(3',4'-methylenedioxy) phenyl-3-phenyl and  $\beta$ -methyl-2(4'-nitrophenyl)-3-phenyl chromones showed activity to *B. subtilis* at 100 ppm. The specific activity of these linear compounds to *B. subtilis* is noteworthy.

Of the twenty-three angular (7,8)- $\alpha$ -pyronochromones screened, 7,8- $\alpha$ -pyrono-2-phenyl-3-methyl chromone exhibited activity to all the three bacteria at 100 ppm and to *S. aureus* and *E. coli* at 20 ppm. The corresponding isomer, 7,8- $\alpha$ -pyrono-2-methyl-3-phenyl chromone was effective to only *B. subtilis* at 100 ppm. The other compounds active are 7,8- $\alpha$ -pyrono- $\alpha$ ,3-dimethyl-2-phenyl and 7,8- $\alpha$ -pyrono- $\alpha$ ,3-dimethyl-2-(4'-nitro) phenyl chromones to *S. aureus* and *E. coli* at 100 ppm and inactive on further dilutions.

The authors are thankful to Sri A. Annaji Rao for elemental analysis and one of the authors (MVL) is grateful to C.S.I.R. for the award of a Junior Research Fellowship.

Chemistry Department, M. VIJAYA LAKSHMI.  
O.U., Hyderabad-7, N. V. SUBBA RAO.  
August 7, 1972.

1. Vijaya Lakshmi, M. and Subba Rao, N. V., *Indian J. Chem.*, 1969, 7 (4), 410.
2. Desai R. D. and Ekhlal, M., *Proc. Indian Acad. Sci.*, 1938, 8A, 567.
3. Deliwala, C. V. and Shah, N. M., *J. Chem. Soc.*, 1939, p. 1250.
4. Shah, N. M. and Deliwala, C. V., *Proc. Indian Acad. Sci.*, 1942, 16 A, 387.
5. DaRe, P. and Verlicchi, L., *Ann. Chem.*, 1960, 50, 1642.
6. Row, L. R. and Seshadri, T. R., *Proc. Indian Acad. Sci.*, 1957, 34 A, 187.
7. Bigger, J. W., *Handbook of Bacteriology*, Baillere, Tindall and Cox, London, 1943, 35.

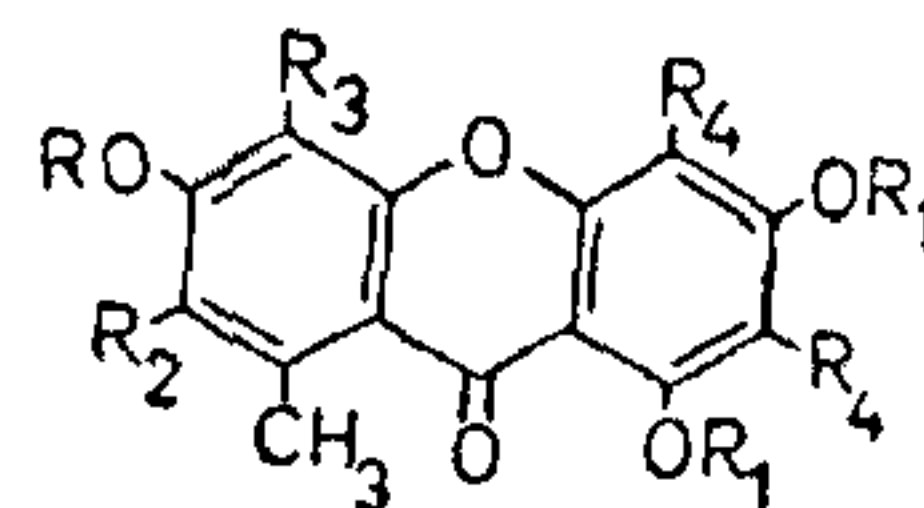
### A NEW SYNTHESIS OF THIOPHANIC ACID

THIOPHANIC acid is an interesting naturally occurring chloro-xanthone derivative of lichen origin<sup>1,2</sup>. Its structure as 2,4,5,7-tetrachloro-1,3,6-trihydroxy-8-methylxanthone (I) was recently proposed by Huneck<sup>3</sup> based largely on spectral properties.

Jayalakshmi, Neelakantan and Seshadri<sup>4</sup> confirmed this structure by reporting its first synthesis. In this synthesis, 1,3-dihydroxy-6-methoxy-8-methylxanthone<sup>5</sup> (II) was fully methylated and then chlorinated to yield compound (III) which was finally demethylated to thiophanic acid (I). More recently other reports<sup>6,7</sup> on the synthesis of this natural product have also appeared.

In the course of our studies on the synthesis of other naturally occurring xanthenes, we have been able to prepare thiophanic acid (I) by following a route which is capable of giving partially dechlorinated thiophanic acid derivatives also. In this, 3,5-dichloroeverninic acid (3,5-dichloro-2-hydroxy-4-methoxy-6-methylbenzoic acid) and phloroglucinol are condensed together in the presence of phosphorus oxychloride and anhydrous zinc chloride. The resulting product, viz., 5,7-dichloro-1,3-dihydroxy-6-methoxy-8-methylxanthone (IV) (m.p. 280-82°; reddish green ferric reaction) is fully methylated with dimethyl sulphate and potassium carbonate in acetone solution to the methyl ether (V) (m.p. 205-07°; negative ferric reaction) which undergoes dichlorination with chlorine (2.5 moles) in carbon tetrachloride solution yielding 2,4,5,7-tetrachloro-1,3,6-trimethoxy-8-methylxanthone (thiophanic acid trimethyl ether) (III) (m.p. 215-16°), identical with an authentic sample. Demethylation of this product (III) with anhydrous aluminium chloride and benzene<sup>4</sup> yields thiophanic acid (I) (m.p. 240-41°) having all the properties described earlier<sup>3,4</sup> for this compound.

Similar condensation of 5-chloroeverninic acid with phloroglucinol gives 7-chloro-1,3-dihydroxy-6-methoxy-8-methylxanthone (VI) (m.p. 299-301°; green ferric reaction) which is also converted into thiophanic acid (I) (m.p. and mixed m.p. 240-41°) by complete methylation to (VII) (m.p. 192-93°; negative ferric reaction), followed by chlorination with chlorine (3.5 moles) in carbon tetrachloride solution and final demethylation.



- (I) R = R<sub>1</sub> = H; R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = Cl
- (II) R = CH<sub>3</sub>; R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H
- (III) R = R<sub>1</sub> = CH<sub>3</sub>; R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = Cl
- (IV) R = CH<sub>3</sub>; R<sub>1</sub> = R<sub>4</sub> = H; R<sub>2</sub> = R<sub>3</sub> = Cl
- (V) R = R<sub>1</sub> = CH<sub>3</sub>; R<sub>2</sub> = R<sub>3</sub> = Cl; R<sub>4</sub> = H
- (VI) R = CH<sub>3</sub>; R<sub>1</sub> = R<sub>3</sub> = R<sub>4</sub> = H; R<sub>2</sub> = Cl
- (VII) R = R<sub>1</sub> = CH<sub>3</sub>; R<sub>2</sub> = Cl; R<sub>3</sub> = R<sub>4</sub> = H
- (VIII) R = CH<sub>3</sub>; R<sub>1</sub> = H; R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = Cl



When this work was almost completed, the paper by Ollis and coworkers<sup>7</sup> appeared in which a new synthesis of thiophanic acid (I) was described. In their method, 5,7-dichloro-1,3-dihydroxy-6-methoxy-8-methylxanthone (IV) was chlorinated with sulphuryl chloride to thiophanic acid-6-methyl ether (VIII) which was demethylated with pyridine hydrochloride to thiophanic acid (I). However the present method is somewhat different from that followed by the British workers<sup>7</sup> and hence our results are reported in this communication.

The authors wish to thank the University Grants Commission for the award of a Junior Research Scholarship to one of them (N. T.).

Department of Natural Products Chemistry and Physical Chemistry,  
Madurai University,  
Madurai-2, May 4, 1972.

S. NEELAKANTAN.

N. THILLAICHIDAMBARAM.

1. Hesse, O., *J. pr. Chem.*, 1898, 58, 465.
2. Kennedy, G., Breen, J., Keane, J. and Nolan, T. J., *Sci. Proc. roy. Dublin Soc.*, 1937, 21, 557.
3. Huneck, S., *Tetrahedron Letters*, 1966, No. 30, 3547.
4. Jayalakshmi, V., Neelakantan, S. and Seshadri, T. R., *Curr. Sci.*, 1968, 37, 196.
5. Grover, P. K. and Shah, R. C., *J. sci. industr. Res. (India)*, 1956, 15 B, 629.
6. Santeesson, J., *Ark. Kemi*, 1969, 30, 449.
7. Arshad, M., Devlin, J. P. and Ollis, W. D., *J. Chem. Soc., C*, 1971, p. 1324.

### STUDY OF THE GARNETS FROM SAKARSANITES, SAKARSANAHALLI. KOLAR DISTRICT, MYSORE STATE

AN interesting series of metamorphic rocks consisting of secondary augite rocks, sillimanite-quartz schists, manganiferous limestones, garnetiferous pyroxene schists etc., occurring in the vicinity of Sakarsanahalli (Lat. 12° 50' N; Long. 78° 15' E), Kolar District, have attracted the attention of many geologists from Mysore. Jayaram (1922) gave the name Sakarsanite to these metamorphic rocks and compared them to gondites and kodurites and considered them to be metamorphosed sediments. Sampath Iyengar (1931) regarded the series as merely altered and metamorphosed hornblende schists—"the Tarurites". This view was supported by Ramachandra Rao and Sripada Rao (1934). Fermor (1938), however, could not agree with these views; he pointed out the similarity between the rocks of this region and the rocks of the Sausar series and considered that it is at least in part sedimentary. Rama Rao (1940) who could not find detailed evidences indicating their origin com-

pared these rocks with other interesting metamorphic rocks like Bidalotite, Kodamite, Bandite occurring in the State of Mysore. He considered these rocks to represent the remnants of the intensely metamorphosed phases of original sediments.

With a view to re-examine the rocks of this region particularly from the point of view of mineralogy and petrology, the author undertook an investigation of the individual minerals reported to occur in these rocks. As a first step, the garnets occurring in these metamorphic rocks have been studied by chemical, optical and X-ray methods. The results of this investigation are reported here.

Garnets are common in the Sakarsanites, especially in the garnet-diopside rocks and banded Tarurites. The garnets vary widely in their size from big trapezohedral crystals sometimes measuring 5 cm across to tiny crystals that can hardly be recognised by naked eye. Whatever may be their size and association, they are deep brown in colour with trapezohedral outline. The fresh unaltered crystals are bright and transparent. Weathered ones show a pale brown to dark brown colour, almost becoming opaque. In thin sections they show the rounded outline characteristic of the trapezohedrons, isotropic and pink to yellowish brown in colour. Often the crystals show cracks, and inclusions of quartz. The grains of quartz were carefully separated from garnets by heavy liquids and hand-picked crop was used for chemical analysis, X-ray studies and the determination of specific gravity and refractive index. These data are given in Table I. The chemical, optical and X-ray characters of the garnet under study

TABLE I

*Chemical composition, physical, optical and X-ray data for the garnet from Sakarsanahalli*

Percentages by weight:		Molecules	
SiO <sub>2</sub>	.. 37.40	Spessartite	61.37
Al <sub>2</sub> O <sub>3</sub>	.. 19.02	Almandite	3.33
Fe <sub>2</sub> O <sub>3</sub>	.. 7.20	Pyrope	17.65
FeO	.. 1.43	Andradite	17.65
CaO	.. 5.60		
MgO	.. 4.03		
MnO	.. 24.79		
TiO <sub>2</sub>	.. 0.16		

Analyst: A. M. Pathan.

Specific gravity: 3.833

Refractive Index: 1.795

Unit cell dimension (a): 11.623 Å

Structural formula on the basis of 24 (O):

Si<sub>6</sub> 763 (Mg F<sup>+</sup> Ca Mn Na K)<sub>6-52</sub> (Al Fe<sup>++</sup> Ti)<sub>5</sub> 06

shows that it is essentially a spessartite with subordinate amounts of pyrope and andradite. Spessartite, which is a less common species, is known to be associated frequently in manganese-rich assemblages, with rhodonite, pyroxmangite, tephroite, etc.