STUDIES ON THE SYNTHESIS AND SPECTROSCOPY OF POLYMETHYLAURINS Part 2

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ポリメチールオーリンの合成とそのスペクトル その2

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OUTLINE

The authors Prepared three new kinds of Polrmethyl aurins in crystalline forms. And a few data were taken about NMR and others.

1 INTRODUCTION

One of the authors published part 1 of the same Studies and described some new methylaurins. This time the authors could prepare a few more new kinds of polymethylaurins using, 2,6-diisopropylphenol and others as raw materials. They were prepared by the same method as in part 1 and were examined as usual by elementary analysis, UV and V spectroscopy, some of them by NMR spectroscopy. V spectroscopy was very useful to get some relationships between them, i.e. the relationships between the absorption and the number of CH_3.

2 SYNTHESIS OF POLYMETHYLAURINS

An example of synthesis is introduced below. 1g of 2,6-dimethoxyphenol was taken, 3.5ml of 33% NaOH, 3ml of 50% trichloroacetic acid added and was heated at about 100℃ on a waterbath for an hour. Then the solution was neutralized with dil. HCl. The separated pigment was washed well with water. Dissolved in ethylalcohol it was developed on an alumina column chromatogragh. The column was passed through with a mixed solvent of ethylalcohol:water (2:1) · The pigment layer was developed down and evaporated. yield: 3 %.

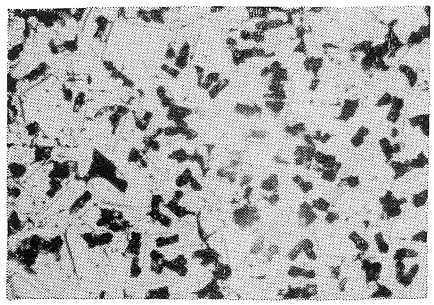
M.P and Elementary analysis

Compound	M.P ℃	Molecular formula	C% Calc.	C% Found	H% Calc.	H% Found
3, 5, 3,′ 5,′ 3,″ 5″-hexaisoprophyl phenolaurin	245	$C_{37}H_{50}O_3$ (H_2O)	79.3	79.0	9.3	
3, 3,′ 3″-trimethyl 5, 5.′ 5″-tri-tert-butyl aurin	150-152	$C_{34}H_{44}O_3$	81,6	81.0	8.8	
3, 5, 3,′ 5,′ 3,″ 5″-hexa methoxyaurin	>300	$C_{25}H_{26}O_9$ ($2H_2O$)	59.5	60.0	6.0	

The pigments prepared from symmetrical polymethylphenol gave usually clear crystalline forms. Some photos are shown below.

3 NMR SPECTROSCOPY

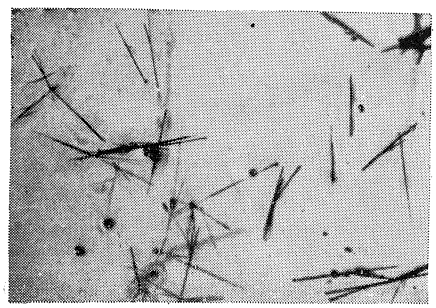
Methyl radicals seem to have caused the peak 4 in Fig.1 without any shift by OH and CO in the molecule. According to the same reason tertbutyl radical seems to have it's peak 5 in one place with no shift. The area ratio of peak 4 and 5 is 1:3, which is proportional to the hydrogen numder of both methyl and tert-butyl radicals. As seen in Fig.2, two isopropyl radicals in one moleeule have their peaks at 4 and 5 according to the interfering effects of both OH and CO.



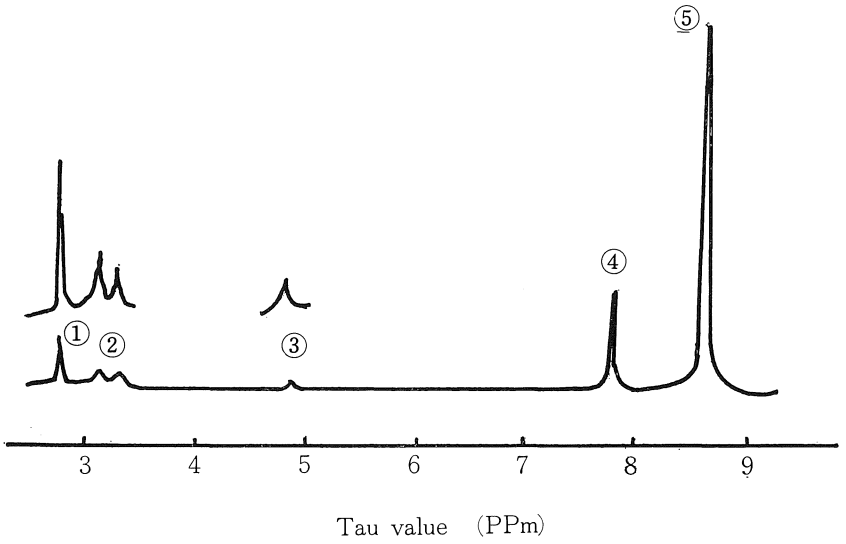
1 Microscopic photos of polymethyl phenol-aurin crystals (×60)

1) 3,3′,3″-trimethyl, 5,5,′5,″-tritert-butylaurin

2 2) 3,5,3′.5′,3″,5″-hexaisopropylaurin



3 3) 3,5,3′,5′,3″,5″-hexamethoxyaurin



1) $CDCl_3$ 2.75 tau

2) H of benzene ring 3.10

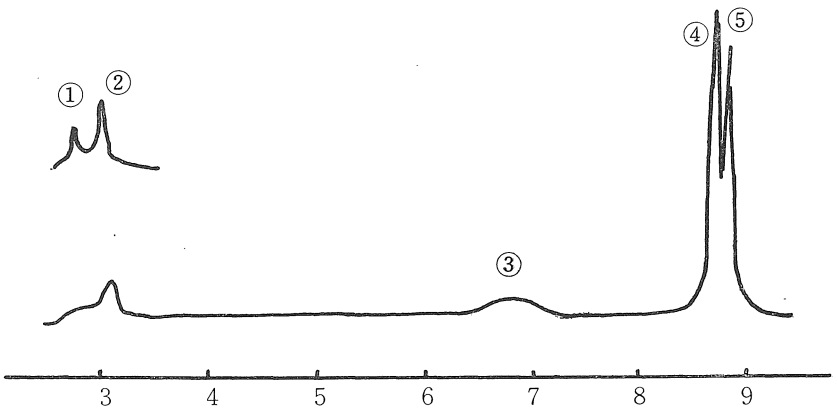
3) -OH 4.82

4) $-CH_3$ 7.80

5) $-\overset{CH_3}{\underset{|}{C}}-CH_3$ 8.66

Solvent: $CDCl_3$ (2%)

Fig.1 NMR Spectrum of 3,3′,3″-trimethyl, 5,5′,5‴-tri-tert-butylaurin



1) $CDCl_3$ 2.75 tau
2) H of benzene ring 3.0
3) -OH, -C 6.8
4) $-C(-CH_3)_2$ (ortho position) of -OH 8.75
5) $-C(-CH_3)_2$ (ortho position) of CO 8.85

Fig.2 NMR Spectrum of 3,5,3′,5′,3″,5″,-hexaisopropylaurin

4 UV and V SPECTROSCOPY

Polymethylaurins including aurin have their characteristic absorptions around 550 mm. But the OCH_3 introduced into the pigment molecule has a tendency to shift the peak to the long wave side.

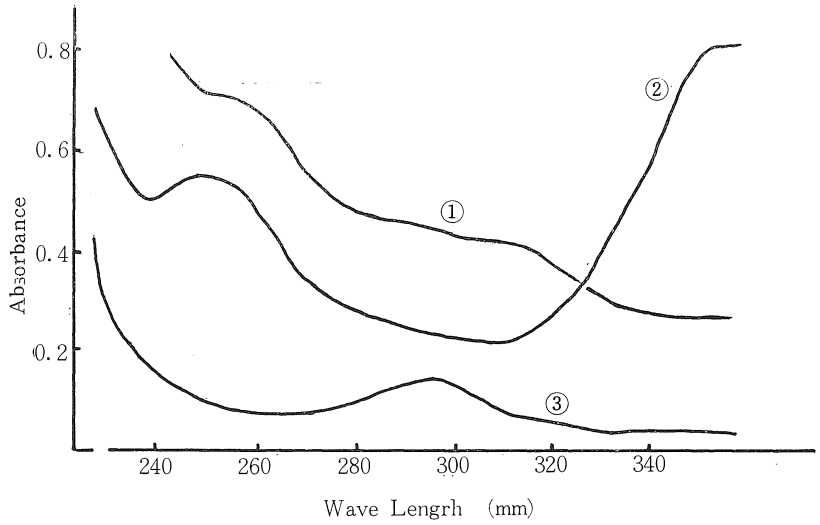


Fig.3 .1 UV Spectra of polymethylaurins
1) 3, 5, 3,′ 5,′ 3,″ 5″-hexamethoxyaurin
2) 3, 3,′ 3,″-trimethyl, 5, 5,′ 5″ - tri-tert-butylaurin
3) 3, 5, 3,′ 5,′ 3,″ 5″ -hexaisopropylaurin NaOH sol. (ph7-10) 0,05 mg／ml (sample)

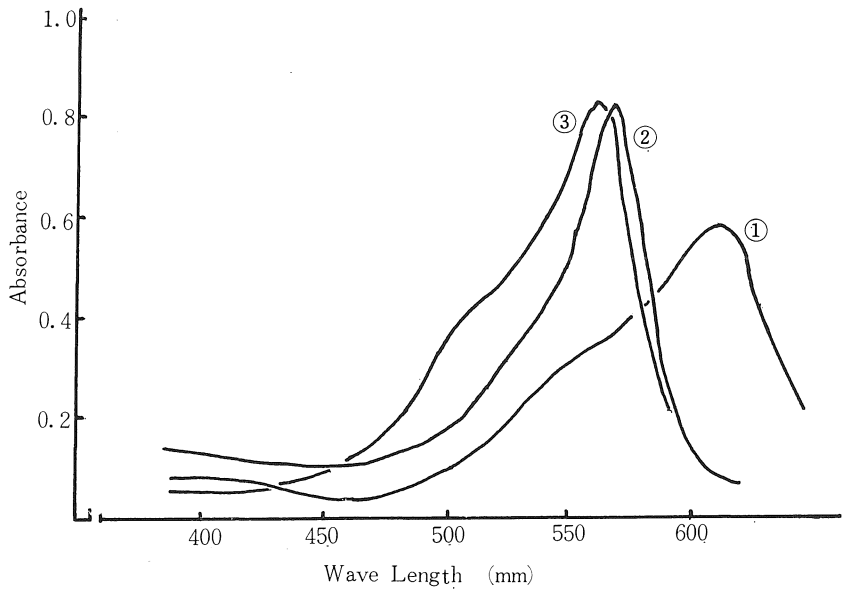


Fig.3 .2 V Spectra of polymethylaurins

5 IR SPECTROSCOPY

The absorption by phenolic OH radical can be observed at 3400 cm and those by CH_3 and OCH_3 radicals at 2900, 1200-1300 cm^{-1} each.

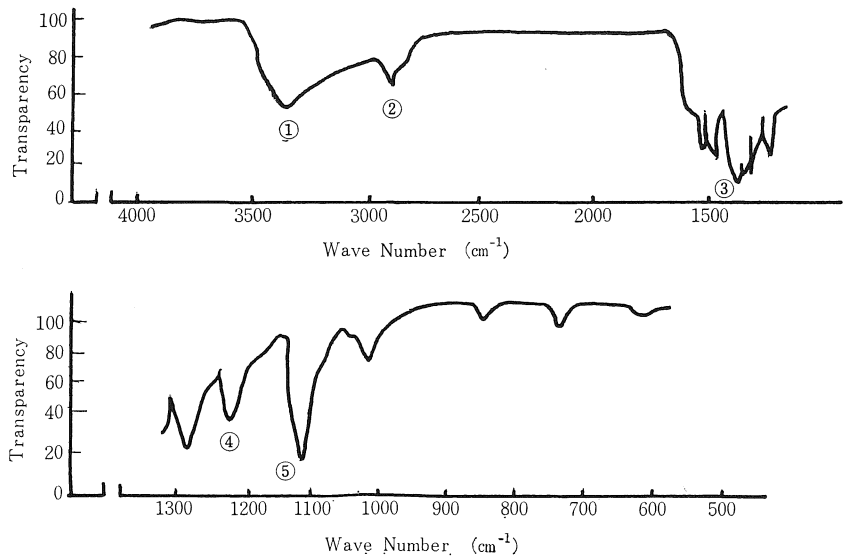


Fig.4 IR Spectrum of 3, 5, 3,′ 5,′ 3,″ 5″ -hexamethoxyaurin

1) 1.v of OH 2) 1.v of CH_3
3) characteristic absorption of benzene ring
4) unsymmetrical 1.v of -C-C-C
5) 1.v of -C-OH

pellet method : kbr 200 mg sample 0.1-0.5 mg

1.v longitudinal vibration

6 Conclusion

In this paper the authors prepared four new kinds of polymethylaurin, i. e. 3, 3′, 3″-trimethoxyaurin, 3, 3′,3″- trimethyl, 5, 5′,5″- tert-butylaurin and 3, 5, 3′, 5′, 3″, 5″- hexaisopropylaurin, These pigments were easily obtained in clear crystalline forms except for the first one. Thier chemical structures were identified by elementary analysis NMR, UV, V and IR spectroscopy.

Acknowledgment

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References

Some parts of this paper were presented at the united meeting of related chemical academic associations in Hokkaido, August 1970.

1) K. Kihara and others: Kogyo Kagaku Zasshi. 73, 2, 110 (1970)
This report was designated as part 1 of Studies on the synthesis and spectroscopy of polymethylaurins.