PART - II

THE STRUCTURES OF XANTHOCHYMOL AND ISOXANTHOCHYMOL

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Garcinia xanthochymus Hook f

It is a medium sized, bushy, evergreen tree, with a straight bole and angular spreading branches arising in tiers. The fruits are yellow when ripe, smooth, globular, 2"-3.5" in diameter, with a prominent beak more or less on one side; seeds 1-4 oblong. The tree is considered to be a native of India and Burma. It is found widely distributed in the lower hill forests of Eastern Himalayas (Assam, Bengal, Bihar and Orissa) and in Bombay, Madras, Mysore, Coorg and Travancore-Cochin. The fruit has a juicy pulp with a pleasant acid flavour and contains approximately 37% pulp. Mahadeviah and Siddappa reported analysis of the pulp, which showed the following values: moisture 83.5%, ash 1.2%, acid (as citric) 4.7%; total soluble solids 12%; reducing sugars 2.6%; ascorbic acid 10 mg% and β-carotene in traces. The pulp made an acceptable yellow squash drink (25% pulp), with an acidic sweet taste similar to that of green tamarind. It is also made into preserves and jams. It can be used in place of tamarind for curries and in the preparation of vinegar. A sherbat made of the dried fruit is given in bilious conditions. The bark is employed by the phakials of the Lakhimpur district of Assam, for dyeing cotton.
Previous work

Earlier, from the fruits of *G. xanthochymus*, Karanjgaokar⁴ of this group had isolated a yellow crystalline compound, xanthochymol. On the basis of the elemental analysis and molecular weight (*M*⁺ 602), it was assigned the molecular formula C₃₀H₅₀O₆. Various colour reactions (Shinoda test, Asahina test, Gibbs test, gossypetone test, conc. sulphuric acid test, etc.) indicate that the compound is neither a flavone nor a xanthone. Absence of a carboxyl group was inferred from its insolubility in aqueous sodium bicarbonate. The UV spectrum of xanthochymol in ethanol shows absorptions at λmax 270 and 224–230 nm. Xanthochymol on hydrogenation over Pd/C catalyst formed a decahydro-derivative. No crystalline derivative of xanthochymol was obtained. However, from the methylation and acetylation experiments the presence of two phenolic hydroxyls was inferred. Ozonolysis of xanthochymol gave formaldehyde and acetone, which were characterised as their 2,4-dinitrophenylhydrazone derivatives. The residue obtained in the ozonolysis experiment was not identified.

Karanjgaokar⁴ had also recorded the NMR spectrum of xanthochymol, but could not derive much information from it, because the spectrum showed broad absorptions.
PRESENT WORK

Xanthochymol isolated by Karanjgaokar's procedure has been submitted to various chromatographic techniques for ascertaining its purity. Thus cellulose, polyamide, silica gel, silica gel impregnated with oxalic acid and alumina (neutral) with different solvent systems have been tried. Cellulose, polyamide and alumina (neutral) proved unsatisfactory and silica gel was found to be the most suitable adsorbent. Two dimensional TLC on silica gel (acetone/pet. ether, 3:7) worked the best. Examination of the old samples of xanthochymol revealed the presence of a slower moving compound, having the same molecular weight as that of xanthochymol, designated as isoxanthochymol.

The petroleum ether extract of the fruits of G. xanthochymus contained mostly a faster moving terpenoid and xanthochymol with small amounts of isoxanthochymol. Chromatography of the petroleum ether extract on a column of silica gel (acetone/pet. ether, 1:9) gave the faster moving terpenoid (1.2%), m.p. 64°. Xanthochymol on purification by repeated crystallisation from pet. ether (60-80°), was obtained as yellow needles, m.p. 135°. Isoxanthochymol crystallised from acetone-pet. ether in pale yellow needles, m.p. 222°. The yields of xanthochymol and isoxanthochymol were respectively 1.9% and 0.5% on the air-dry weight of the fruits.
The molecular formula $\text{C}_{38}\text{H}_{50}\text{O}_6$ for xanthochymol was derived from the molecular weight ($M^+ = 602$) and elemental analysis. It gave a deep green colour with alcoholic ferric chloride and no colouration in the Shinoda test.

Xanthochymol shows in its UV spectrum (Fig. 1, Table 1) absorption at 230 and 276 nm ($\epsilon = 15,700$ and 20,160) in ethanol; but in cyclohexane bands are seen at 264 and 364 nm ($\epsilon = 12,270$ and 9,810). The difference in the maxima by using these two solvents is not understood clearly and can be attributed to the solvent association when ethanol is used. Morellin$^5$ shows well defined maxima at 236, 268.5 and 360 nm, both in ethanol and cyclohexane. From this it appears that xanthochymol has an extended conjugated chromophore as in morellin. The IR spectrum of xanthochymol (Fig. 2) shows strong absorption at 3200-3400 cm$^{-1}$, indicating the presence of phenolic hydroxy groups and in the carbonyl stretching region it shows three absorptions at 1715, 1660(sh) and 1630 cm$^{-1}$. The band at 1715 cm$^{-1}$ is not due to a carboxylic acid group, because the compound is completely insoluble in aqueous sodium bicarbonate and fails to respond to common colour reactions characteristic of a carboxylic acid function. This bond can be attributed most probably to a six-membered cyclic ketone.$^6,7$ The strong band at 890 cm$^{-1}$ can arise from the CH$_2$ out-of-plane bending vibrations of a terminal methylene group$^8$ and this conclusion finds support in the absorption at 3079 cm$^{-1}$ for C-H stretching vibrations of $\text{C}=\text{CH}_2$ grouping.$^9$

The NMR spectrum of xanthochymol in CDCl$_3$ (Fig. 3; Table 3) (chemical shifts on the $\tau$ scale) shows three aromatic
FIG. 1

- Dotted line: XANTHOCHYMOL IN ETHANOL
- Dashed line: XANTHOCHYMOL + NaOH
- Solid line: XANTHOCHYMOL IN CYCLOHEXANE

\[ \varepsilon \times 10^{-4} \]

\[ \lambda, \text{nm} \]

220 240 260 280 300 320 340 360 380 400

FIG. 1
<table>
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<th>Compound</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ nm (log $\varepsilon$)</th>
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<td>Ethanol</td>
<td>231(4.0), 277(4.0)</td>
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<td>Ethanol</td>
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<tr>
<td>(-) Trans-isohumulone$^6$</td>
<td>Methanol/H$^+$</td>
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<td>$^\cdot$/HO$^-$</td>
<td>251(4.2), 270sh(4.1)</td>
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<td>Methanol/H$^+$</td>
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<td></td>
<td>Ethanol/HO$^-$</td>
<td>251.5(4.14), 277(4.09), 357(4.29)</td>
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</table>
FIG. 3  NMR SPECTRUM OF XANTHOCHYMOL IN CDCl₃
hydrogens: an ortho-coupled doublet ($J = 9$ Hz) at 3.42 and a meta-coupled doublet ($J = 2$ Hz) overlapping with a quartet at 2.85-3.05. This is very characteristic of a 1,2,4-trisubstituted benzene ring. Further, these chemical shifts suggest the presence of a 3,4-dihydroxybenzoyl group in the molecule. The NMR spectrum also indicates the presence of three vinyl hydrogens (broad triplet at 5.1); the broad signals at 5.3 and 5.5 due to the protons of a terminal methylene group; seven methyl groups between 8.0 to 8.4 and the two 3-proton singlets at 8.8 and 8.95 which can be assigned to two methyl groups on a saturated carbon attached to an oxygen as in a 2,2-dimethylchroman. The remaining thirteen hydrogens are seen as a complex absorption in the region between 7.2 to 8.5 representing methylene groups (including allylic) and methine protons.

Catalytic hydrogenation gave an octahydroxanthochymol ($M^+ = 610$) indicating the presence of four ethylenic double bonds in xanthochymol. Karanjgaokar reported the formation of a decahydro derivative on the basis of hydrogen uptake and not confirmed by its mass spectrum. The UV spectrum (Table 1) shows the same maxima as xanthochymol, suggesting that the chromophore remains intact.

Xanthochymol forms two trimethyl ethers when methylated using either dimethyl sulphate or diazomethane. The two trimethyl ethers have the same Rf value on silica
gel TLC and are resolved only on neutral alumina. They were obtained in the pure form by separating on a column of neutral alumina (Brockmann grade I) using pet.ether/benzene (1:1) as the eluent. Both the methyl ethers have been obtained as amorphous powders, and all attempts to get them in crystalline form proved to be fruitless. In the NMR spectrum (Fig.4 and 5; Table 3) both the ethers show three aromatic hydrogens at 2.35 (d, J=2 Hz), 2.75 (d, J=9 and 2 Hz) and 3.25 (d, J=9 Hz). The methoxyls appear as two singlets at 6.05 and 6.35 integrating for six and three protons respectively. When the mixture of the two trimethyl ethers was hydrolysed with 5% ethanolic sodium hydroxide, a single dimethyl ether was obtained. The NMR spectrum of the dimethyl ether (Table 3) shows three aromatic hydrogens as in xanthochymol and a two-methoxyl singlet at 6.12. The singlet at 6.35 in the spectra of the trimethyl ethers has disappeared, but other parts of the spectra remain unchanged. These observations reveal the presence of a vinylogous ester grouping probably derived from an enolised β-diketonic function. A green colouration with alcoholic ferric chloride in the absence of an chelated hydroxyl suggests a catechol group, confirmed by the formation of a methylene ether with methylene iodide and anhydrous potassium carbonate in boiling acetone, and of a carbonate with phosgene. The methylene derivative (Fig.6; Table 3) shows
FIG. 4 NMR SPECTRUM OF XANTHOCHYMOL TRIMETHYL ETHER A IN CDCl₃
FIG. 5 NMR SPECTRUM OF XANTHOCHYMOL TRIMETHYL ETHER B IN CDCl₃
FIG. 6 NMR SPECTRUM OF XANTHOCHYMOL METHYLENE ETHER IN CCl₄
a 2-proton singlet at 4.0, characteristic of a methylene-dioxy group. The carbonate shows the expected absorption at 1840 cm\(^{-1}\) in the IR spectrum. These results, in combination with the NMR spectral data, lead to a 3,4-dihydroxy-benzoyl moiety in xanthochymol. The mass spectra of xanthochymol and its derivatives support such a formulation.

Xanthochymol shows a fragment ion at m/e 137 (C\(_7\)H\(_5\)O\(_3\); 71.8%); the corresponding ion at m/e 165 is seen in both the di- and trimethyl ethers.

Octahydroxanthochymol, like xanthochymol formed two trimethyl ethers, which were separated on a neutral alumina column using pet.ether/benzene (1:1) as the eluent.

Isoxanthochymol (m.p. 222°) is isomeric with xanthochymol (C\(_{38}\)H\(_{50}\)O\(_6\)), the colour reactions are very similar. The mass spectrum shows almost the same fragmentation pattern as xanthochymol. The UV spectrum (Table 1) shows bands at 232, 275 and 312(sh) nm (\(\epsilon\) 16,430; 18,880 and 8,484). On addition of alkali it showed similar bathochromic shift, therefore it must be having the same chromophore as in xanthochymol. The band at 1720 cm\(^{-1}\) in the IR spectrum indicates a six membered cyclic ketone and the one at 1665 cm\(^{-1}\) is possibly due to an \(\alpha,\beta\)-unsaturated carbonyl. There is no band at 1630 cm\(^{-1}\), but a weak band at 1650 cm\(^{-1}\) indicates either a highly conjugated carbonyl or the C=C stretching vibrations of the
olefinic bonds. The bands at 1600 and 3300-3400 cm\(^{-1}\)
are due to aromatic C=C stretching and O-H stretching
vibrations respectively.

The NMR spectra of xanthochymol and isoxanthochymol
have many common features, but there are also significant
differences. Like xanthochymol, isoxanthochymol (Fig. 7;
Table 3) shows three aromatic protons at 2.9 (d, \(J=2\) Hz),
3.07 (q, \(J=9\) and 2 Hz) and 3.34(d, \(J=9\) Hz), characteristic
of a 3,4-dihydroxybenzoyl group, and there is a broad
3-proton triplet at 5.1 due to vinyl protons. Two methyls
on a carbon attached to an oxygen as in a 2,2-dimethyl
chroman\(^\text{10}\) are located at 8.8 and 8.95 (singlets). However,
the broad signals at 5.3 and 5.5 due to a terminal methylene
group in xanthochymol are not seen in isoxanthochymol. Two
methyl groups on saturated carbon appear at 9.12 and 9.17
(singlets), not seen in xanthochymol. Six vinyl methyls
(instead of seven) are seen at 8.4-8.47. The remaining
twelve protons show a complex absorption between 7.7 to
8.5 representing methylene, allylic methylene and methine
protons.

When hydrogenated in ethanol using 10% palladised
charcoal, isoxanthochymol formed a hexahydro derivative.
These three ethylenic bonds are not in conjugation as shown
by the identical UV spectra of isoxanthochymol and hexa-
hydroisoxanthochymol (Table 1). In the mass spectra of
FIG-7  NMR SPECTRUM OF ISOXANTHOCYMOLOM IN DMSO (D_6) + CDCl_3
isoaxanthochymol and hexahydroisoaxanthochymol, the fragment ion at m/e 137 characteristic of a 3,4-dihydroxybenzoyl moiety is observed. The methyl ethers show the corresponding ion at m/e 165 (base peak in both compounds).

Methylation of isoaxanthochymol with dimethyl sulphate and potassium carbonate yielded an alkali stable dimethyl ether, showing the absence of an enolisable hydrogen postulated in xanthochymol. The NMR spectrum of the dimethyl ether (Fig.8, Table 3) shows two methoxyls at 6.12 and 6.17, and three aromatic protons at 2.59 (d, J=2 Hz), 3.0 (q, J=9 and 2 Hz) and 3.37 (d, J=9 Hz) due to 3,4-dimethoxybenzoyl group. The 3-proton complex multiplet at 5.1 must be due to vinyl hydrogens. The singlets at 8.29 and 8.4, each integrating for nine protons represent the six vinylic methyls. The methyls of the chroman ring are seen at 8.79 and 8.87, and the methyls on a saturated carbon are seen at 9.05 and 9.1 as in the parent compound.

On acetylation isoaxanthochymol formed a diacetate. As expected all the three aromatic protons are pulled down-field and appear at 2.54 (q, J=9 and 2 Hz), 2.66 (d, J=2 Hz) and 2.94 (d, J=9 Hz). A singlet at 7.7 integrating for six protons is due to the two acetoxyls (Table 3).

By treatment with DDQ (2,3-dichloro-5,6-dicyanobenzoxo-quinone) isoaxanthochymol formed an ortho-quinone showing
FIG. 8 NMR SPECTRUM OF ISOXANTHOCHYMOL DIMETHYL ETHER IN CCl₄
characteristic absorption bands at 230, 254.5, 275 and 432 nm in the UV spectrum.

To deduce the nature of the olefinic bonds, the dimethyl ether of isoxanthochymol \( \text{C}_{40}\text{H}_{54}\text{O}_{6} \) was ozonised at 0° in ethyl acetate. The ozonide was then decomposed with Jones reagent\(^{11} \) in acetone at 5°, and the acid thus obtained was esterified with ethereal diazomethane. From the elemental analysis of this ether-ester (V) and the molecular weight \( M^+ = 642 \) the molecular formula \( \text{C}_{34}\text{H}_{42}\text{O}_{12} \) was deduced. The NMR spectrum of (V) (Fig. 9) shows a singlet at 6.05 for six protons assigned to two methoxys of a 3,4-dimethoxybenzoyl group in combination with three aromatic protons at 2.3, 2.37 and 3.2. Additional signals at 6.25, 6.3 and 6.37, each integrating for three protons, represent three carbomethoxys. Therefore (V) must be a trimethyl ester and the parent acid must be a tricarboxylic acid having the molecular formula \( \text{C}_{31}\text{H}_{36}\text{O}_{12} \). The three carboxyl groups must have been generated by the oxidation of three olefinic bonds resulting in the loss of nine carbon atoms. In another experiment the ozonide was hydrogenated on palladized carbon and the volatile compounds were distilled and collected in 2,4-dinitrophenylhydrazine solution, when 2,4-dinitrophenylhydrazone of acetone was obtained.

The results of these experiments can be well explained by assuming the presence of three 3,3-dimethylallyl groups in isoxanthochymol.
FIG. 9. NMR SPECTRUM OF ISOXANTHOCYMYL TRICARBOXYLIC ACID PENTAMETHYL ETHER-ESTER (V) IN CDCl₃
From the above results it is clear that xanthochymol and isoxanthochymol are very closely related and differ mainly in two features (1) xanthochymol has an additional double bond (terminal methylene group), and (2) forms two trimethyl ethers which can be easily hydrolysed to a single dimethyl ether, while isoxanthochymol forms only a dimethyl ether. Further, the additional two methyl groups on a saturated carbon in isoxanthochymol appearing at 9.12 (3H, s) and 9.17 (3H, s) in the NMR spectrum, and not present in xanthochymol indicates the cyclisation of a C₅-group containing the terminal methylene group of xanthochymol which is absent in isoxanthochymol. The disappearance of the enolisable hydrogen in isoxanthochymol shows its involvement in the cyclisation.

In the mass spectra of xanthochymol and isoxanthochymol the base peak at m/e 69 (C₅H₅) is probably due to the cleavage of an isoprenyl group which is substituted on a saturated carbon.¹⁰,¹² The loss of C₁₀H₁₆ from the molecular ion, involving hydrogen transfer, and a prominent loss of C₁₀H₂₀ in the spectrum of octahydroxanthochymol suggest the presence of a C₁₀H₁₇ side chain adjacent to a carbonyl group.

From the NMR and mass spectral data, it can be concluded that xanthochymol and isoxanthochymol are derived from a C₁₃ skeleton to which five isoprenoid units are
attached. The \( C_{13} \) skeleton can be a benzophenone or a xanthone or one of their hydrogenated derivatives as in the morellin pigments. The overwhelming evidence for the presence of a 3,4-dihydroxybenzoyl group in xanthochymol and iso-xanthochymol suggests the absence of a morellin type skeleton. The other alternative appears to be a modified benzophenone in which the shikimate derived ring remained intact (3,4-dihydroxybenzoyl group) and the acetate derived ring might have been prenylated. The only naturally occurring prenylated benzophenone is bromianone (I), isolated from G. hombronianii.

It appears likely that xanthochymol may also have a similar skeleton as that of bronianone. However, there is no proof for the presence of a bicyclo[2.2.2] octenone system in xanthochymol, as suggested in bronianone. The two methyls of the tetrahydrofuran ring of bicyclo[2.2.2]octenone system are seen at 8.25 and 8.52 in morellin and its analogues; but xanthochymol shows two methyls on a saturated carbon at 8.8 and 8.95 and not below 8.5. These methyl signals can well be assigned to the two methyl groups of a 2,2-dimethylchroman ring as described earlier. If maclurin (II) is considered as a biogenetic precursor for many of the tetrahydroxyxanthones, which are frequently encountered as their methyl ethers or C-prenylated derivatives; it is most likely that the \( C_{13} \) unit in xanthochymol may also have been derived from maclurin in which the B-ring remains intact,
OH

(III)

Me (I)

\[ R^1 = (\text{CH}_2-\text{CH} = \text{C} - \text{CH}_2)_2 - \text{CH}_2 - \text{CH} = \text{CMe}_2 \]

Me

\[ R^2 = \text{CH}_2 - \text{CH} = \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CMe}_2 \]

(II)

(III)

(IV) \( R = \text{H} \)

Dimethyl ether \( R = \text{Me} \)  Dibromosylate \( R = -\text{SO}_2\)
while the acetate derived phloroglucinol ring A becomes the target of attack by five "active isoprene" groups resulting in the partial structure (III) for xanthochymol. $R_1$, $R_2$ and $R_3$ represent one C$_{10}$ and two C$_5$ units. The acetate derived phloroglucinol unit being attacked by the isoprene units is of common occurrence in many other natural products such as hop pigments.$^{16,17}$

The UV spectrum of xanthochymol is also in agreement with the proposed partial structure (III). The $\beta$-triketones$^{18}$ show characteristic absorption bands at 230-235 and 275 nm. Some examples of $\beta$-triketones are given in Table 1. Smith$^{19}$ has studied UV and IR spectra of 2-acetylcyclohexane-1,3-dione. In the UV spectrum it shows absorption maxima at 235 and 275 nm ($\varepsilon_{14},700$ and $11,600$) characteristic of the enolised $\beta$-triketone system. According to him the band at 235 nm is associated with the $\alpha,\beta$-unsaturated carbonyl group$^{20}$ and the band at 275 nm is associated with the conjugated diene chromophore contained in one ring.$^{21}$ UV spectrum of xanthochymol shows these characteristic absorption bands.

As it was very difficult to arrive at the complete structure of xanthochymol and isoxanthochymol, their di-p-bromobenzene sulphonates have been prepared with a view of obtaining their X-ray analysis. However, only isoxanthochymol gave better crystalline di-p-bromobenzene sulphonate in the
DIMETHYL ETHER $R = \text{Me}$

DIBROSYLATE $R = \text{SO}_2\text{-Br}$

(V)

(VI) $R = \text{H}$

(VII)  

(VIII)
form of colourless long prisms and its X-ray structure (IV) was determined by Dr. Palmer of the Western Regional Research Laboratory, Berkeley. From the structure (IV) of isoxanthochymol it was possible to locate \( R^1 \), \( R^2 \) and \( R^3 \) in xanthochymol and has been represented by structure (VI).

All the spectral evidences fully support structures (VI) and (IV) for xanthochymol and isoxanthochymol respectively.

**Biogenesis of xanthochymol**

Hydroxybenzophenones are believed to result by the condensation of shikimate and acetate derived moieties.\(^{22}\) The acetate derived acyclic \( \beta \)-triketide may condense with a hydroxybenzoic acid (derived from shikimate unit) to give the corresponding benzophenone. Likewise maclurin (II) is derived by the condensation of 3,4-dihydroxybenzoic acid with an acyclic \( \beta \)-triketide. Scheinmann et al.\(^{23}\) have demonstrated the significance of maclurin in xanthone biosynthesis by a statistical analysis of xanthones in higher plants. Prenylation of both A and B rings of (II) are involved in the biosynthesis of morellin, but prenol groups attack only the A ring in the biosynthesis of xanthochymol (VI) and isoxanthochymol (IV). The hop phenols, humulone (VII) and lupulone (VIII) are the examples of prenylation of the acetate derived acyclic \( \beta \)-triketide.

Thus the intermediate (IX) obtained by the prenylation of (II) can react with two more prenol groups as indicated.
Loss of the proton (Ha) from the methyl group or the proton (Hb) can lead to xanthochymol or isoxanthochymol respectively.

**Mass spectral fragmentation of xanthochymol and isoxanthochymol**

Accurate mass measurements of the molecular ion (m/e 602) revealed the molecular formula, $C_{38}H_{50}O_6$, for xanthochymol. Xanthochymol and isoxanthochymol show base peak at m/e 69 ($C_5H_9$), characteristic of a isoprenyl group substituted on a saturated carbon.\(^{10,12}\) The process involving loss of a single $C_5H_9$ unit to give an ion at m/e 533 (3.3%) is not predominant as indicated by its less intensity. However, the loss of 137 u from the molecular ion to give an intense peak at m/e 465 ($C_{28}H_{33}O_6$; 33.8%) is quite appreciable. High resolution data (Table 2) for the ion at m/e 137 revealed the possibility of both $C_{10}H_{17}$ and $C_7H_5O_3$ corresponding to 3,4-dihydroxybenzoyl cation, which are in the ratio of 10:1. This ratio is not retained in the spectra of methyl ethers, and the ion at m/e 165 (3,4-dimethoxybenzoyl cation) and m/e 137 due to $C_{10}H_{17}$ side chain are seen in the ratio of 2:1. The ion at m/e 466 ($C_{28}H_{33}O_6$; 19.7%) is formed by the transfer of a $\beta$-hydrogen from the $C_{10}$-side chain to the carbonyl function (McLafferty rearrangement). This reaction becomes more intense in octahydroxanthochymol as indicated by the base peak at m/e 470 resulting by a loss of $C_{10}H_{20}$ from the molecular ion.
TABLE 2
High resolution data on xanthochymol

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<td>121.10173</td>
</tr>
</tbody>
</table>

High resolution data on xanthochymol trimethyl ether.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Elemental composition</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>507</td>
<td>C_{31}H_{39}O_{6}</td>
<td>507.2709</td>
<td>507.27467</td>
</tr>
<tr>
<td>383</td>
<td>C_{22}H_{23}O_{6}</td>
<td>383.14947</td>
<td>383.1581</td>
</tr>
<tr>
<td>245</td>
<td>C_{14}H_{13}O_{4}</td>
<td>245.08139</td>
<td>245.08513</td>
</tr>
<tr>
<td>165</td>
<td>C_{9}H_{9}O_{3}</td>
<td>165.05517</td>
<td>165.05535</td>
</tr>
<tr>
<td>151</td>
<td>C_{3}H_{7}O_{3}</td>
<td>151.0395</td>
<td>151.04483</td>
</tr>
</tbody>
</table>


CHART I MASS SPECTRAL FRAGMENTATION OF XANTHOCHYMOL

\[
\begin{align*}
\text{m/e 110 (12.6\%)} & \quad \text{m/e 231 (16.9\%)} \\
\text{m/e 81 (21.9\%)} & \quad \text{m/e 341 (23.9\%)} \\
\text{m/e 574 (6.9\%)} & \\
\text{m/e 602 (14\%)} & \quad \text{m/e 342 (7.3\%)} \\
\text{m/e 465 (33.8\%)} & \quad \text{m/e 275 (4.3\%)} \\
\text{m/e 451 (3.5\%)} & \quad \text{m/e 330 (6.2\%)} \\
\text{m/e 109 (16.9\%)} & \quad \text{m/e 343 (11.2\%)} \\
\text{m/e 137 (71.8\%)} & \\
\end{align*}
\]
Loss of CO from the molecular ion is a common feature in the fragmentation of all compounds examined.

Other ions of greater abundance in the spectra of xanthochymol and isoxanthochymol are at m/e 341 and 231. The ion at m/e 341 can arise from the ion at m/e 466 involving either expulsion of C_9H_16 (a retro-Diels-Alder reaction)\textsuperscript{24,25} and a hydrogen radical or successive loss of C_9H_15 and two hydrogen radicals, as shown in Chart 1. These two reactions are characteristic of 2,2-dimethylchromans.\textsuperscript{26-28} A metastable peak at 250 mu is observed for this reaction. As expected the dimethyl ethers and trimethyl ethers show ions at 369 and 383 respectively.

The ion at m/e 231 is seen in the spectra of xanthochymol, isoxanthochymol and their dimethyl and methylene ethers. However, the trimethyl ethers show ion at m/e 245 indicating the presence of one methyl ether group in the ion and probably must have formed by the bond fission \( \leftrightarrow \) to the carbonyl, eliminating dimethoxy benzene moiety. Accurate mass measurements revealed the formula C_{13}H_{11}O_4 for the ion m/e 231 confirming the postulated fragmentation (Charts I and III).

Xanthochymol can enolise to give two structural isomers \((X)\) and \((XI)\). The formation of the isomer \((XI)\) is favoured due to the relatively greater stability obtained
CHART II MASS SPECTRAL FRAGMENTATION OF OCTAHYDROXANTHOCHYMOL

m/e 235 (24.0 %)
m/e 287 (15.0 %)
m/e 344 (15.6 %)
m/e 345 (19.0 %)
m/e 360 (10.5 %)
m/e 361 (3.4 %)
m/e 333 (9.0 %)
m/e 470 (100.0 %)
m/e 469 (50.0 %)
m/e 468 (32.2 %)
m/e 610 (20.3 %)
m/e 348 (16.0 %)
m/e 539 (7.0 %)
m/e 472 (16.0 %)
m/e 137 (60.0 %)

m/e 235 (24.0 %)
m/e 287 (15.0 %)
m/e 344 (15.6 %)
m/e 345 (19.0 %)
m/e 360 (10.5 %)
m/e 361 (3.4 %)
m/e 333 (9.0 %)
m/e 470 (100.0 %)
m/e 469 (50.0 %)
m/e 468 (32.2 %)
m/e 610 (20.3 %)
m/e 348 (16.0 %)
m/e 539 (7.0 %)
m/e 472 (16.0 %)
m/e 137 (60.0 %)

223 A
CHART III MASS SPECTRAL FRAGMENTATION OF XANTHOCHYMOL TRIMETHYL ETHER B

\[ \text{m/e 507 (100.0%)} \]

\[ \text{m/e 644 (90.0%)} \]

\[ \text{m/e 383 (90.0%)} \]

\[ \text{m/e 508 (83.0%)} \]

\[ \text{m/e 384 (55.0%)} \]

\[ \text{m/e 245 (90.0%)} \]

\[ \text{m/e 329 (17.5%)} \]
by hydrogen bonding. On methylation of xanthochymol, the trimethyl ether B has been obtained as a major compound, which has been assigned structure (XIII) and the minor trimethyl ether A is represented by the structure (XII). The difference in the fragmentation of these trimethyl ethers A (XII) and B (XIII) is that the former shows base peak at m/e 165 and the latter at m/e 507, which results by knocking-off of the C_{10}H_{17} side chain to the carbonyl.

The trimethyl ether A shows an intense ion at M-55 (m/e 589), which is characteristic of an isopentenyl group substituted on an unsaturated carbon involving β-cleavage.12

The general mass spectral fragmentation of xanthochymol, octahydroxanthochymol and trimethyl ether B is shown in Charts I, II and III respectively.
MASS SPECTRUM OF XANTHOCHYMOL
The structure of Brobianone

Ollis et al.\textsuperscript{13} have isolated a deep yellow oil, bronianone, \( \text{C}_{43}\text{H}_{50}\text{O}_{6} \), from the stemwood of \textit{Garcinia hombroniana} Pierre and suggested structure (I), mainly based on UV (\( \lambda_{\text{max}} \text{nm (e)} \) 250 (10,350), 278(7000), and 365(6500); IR (\( \lambda_{\text{max}} \text{1720 and 1660 cm}^{-1} \); carbonyl groups); NMR (three aromatic protons at 2.4 (d, \( J = 2 \text{ Hz} \)), 2.74 (q, \( J = 8 \text{ and 2 Hz} \)) and 3.23 (d, \( J = 8 \text{ Hz} \)) characteristic of a 3,4-dihydroxybenzoyl group; five vinyl protons, seven olefinic methyls, sixteen allylic protons and two methyls at 8.92 and 9.23 (s) on a saturated carbon and mass spectral data (an initial loss of \( \text{C}_{10}\text{H}_{17} \) followed by the loss of a \( \text{C}_{14}\text{H}_{24} \) fragment either in a single or in a three step sequence). It formed a trimethyl ether which on alkaline hydrolysis gave a dimethyl ether. It gave a decahydro derivative on hydrogenation in which the chromophore remained unchanged.

In the light of the structure of xanthochymol(VI), \( \text{C}_{38}\text{H}_{50}\text{O}_{6} \), and the very close resemblance between the two ketones in many of their properties, bronianone has been represented by the structure (XIV), differing from (VI) only in the nature of two of the side chains. The initial loss of \( \text{C}_{10}\text{H}_{17} \) followed by the loss of \( \text{C}_{14}\text{H}_{24} \) in the mass spectral fragmentation of bronianone and its ethers is better explained
by (XIV); in (I) $R^1$ will be lost as a C$_{15}$ unit, but in (XIV) the loss of C$_{14}H_{24}$ is expected due to retro-Diels-Alder reaction in the chroman ring. In the NMR spectra of bronianone and its methyl ethers, the two methyl signals at 8.92 and 9.23(s) are at considerably higher field than the methyl signals (8.52 or below) of the tetrahydrofuran ring in morellin and its analogues,$^{14,15}$ but they are much nearer to the methyl signals (8.8; 8.95) of the chroman ring in xanthochymol. Structure (XIV), however, has one vinylic methyl group more, and one methine and one allylic CH$_2$ group less than (I); it is doubtful if a clear choice between the two alternatives can be made on the basis of the 60 MHz spectrum of so complex a molecule.

One reason for Ollis et al. assigning the bicyclo[2.2.2] octenone type structure to bronianone is "an interesting biogenetic relation between the polyisoprenylated 'benzophenone' structure (I) and the polyisoprenylated xanthonoids (the morellin group)". In fact, a biogenetic approach to the structure of bronianone will lead almost inevitably to (XIV). The biogenetic process suggested for xanthochymol (VI), starting from maclurin(II) in which (unlike the biogenesis of the morellin type) the target of prenylation is only the phloroglucinol half, is equally valid for bronianone (XIV). The only difference in the biogenesis of (XIV) is that maclurin (II) is progressively attacked by two prenyl and two geranyl units.
<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR data on:</td>
</tr>
<tr>
<td>A. Xanthochymol</td>
</tr>
<tr>
<td>B. Isoxanthochymol</td>
</tr>
<tr>
<td>C. Xanthochymol dimethyl ether</td>
</tr>
<tr>
<td>D. Xanthochymol methylene ether</td>
</tr>
<tr>
<td>E. Isoxanthochymol dimethyl ether</td>
</tr>
<tr>
<td>F. Xanthochymol trimethyl ether A</td>
</tr>
<tr>
<td>G. Xanthochymol trimethyl ether B</td>
</tr>
<tr>
<td>H. Hexahydroisoxanthochymol dimethyl ether</td>
</tr>
<tr>
<td>I. Octahydroxanthochymol trimethyl ether A</td>
</tr>
<tr>
<td>J. Octahydroxanthochymol trimethyl ether B</td>
</tr>
<tr>
<td>Protons</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>2-H of Ar-ring</td>
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<tr>
<td>5-H of Ar-ring</td>
</tr>
<tr>
<td>6-H of Ar-ring</td>
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<tr>
<td>Three vinyl protons</td>
</tr>
<tr>
<td>Terminal CH2 =CH2</td>
</tr>
<tr>
<td>-O-CH2-O-</td>
</tr>
<tr>
<td>Allylic methylenes</td>
</tr>
<tr>
<td></td>
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<td>Protons</td>
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<tr>
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</tr>
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<td>CH₃COO</td>
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<td>Vinylic methyls</td>
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<td>Methylene and methine protons</td>
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<tr>
<td>Methyls of chroman ring</td>
</tr>
<tr>
<td></td>
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<td></td>
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</tbody>
</table>
Specific rotations of xanthochymol, isoxanthochymol and derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$[\alpha]_D^{29}$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthochymol</td>
<td>143.5°</td>
<td>Chloroform</td>
</tr>
<tr>
<td>Isoxanthochymol</td>
<td>179.2°</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Xanthochymol trimethyl ether A</td>
<td>75.98°</td>
<td>Chloroform</td>
</tr>
<tr>
<td>Xanthochymol trimethyl ether B</td>
<td>23.17°</td>
<td>Chloroform</td>
</tr>
<tr>
<td>Hexahydroisoxyanthochymol</td>
<td>79.41°</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Isoxanthochymol dimethyl ether</td>
<td>105.9°</td>
<td>Chloroform</td>
</tr>
</tbody>
</table>
**EXPERIMENTAL**

**Extraction of Garcinia xanthochymus fruits**

The powdered pulp (3.3 kg) of *Garcinia xanthochymus* fruits was extracted with petroleum ether (60–80°) by percolation for three days. This extract (7.5%) on silica gel TLC showed presence of xanthochymol, isoxanthochymol and a faster moving terpenoid. The above powder was then extracted with acetone and ethanol successively. Acetone extract (4%) was treated with water (1.5 lit.) and filtered. The water insoluble solid was then treated with benzene (2 lit.) and filtered. The benzene-soluble part (56 g) showed on TLC a number of spots in addition to xanthochymol and isoxanthochymol. Benzene-insoluble solid (50 g) gave a red colouration with magnesium powder and hydrochloric acid. Morelloflavone has been isolated from this. The ethanol extract (3%), which gave a red colouration with magnesium and hydrochloric acid, has not yet been examined.

**Isolation of xanthochymol (VI)**

Petroleum ether extract (30 g) was chromatographed on a column of silica gel (500 g) using petroleum ether (60–80°)/acetone as the eluent with increasing polarity. After removal of the oil (a terpenoid; 5 g), the fractions containing xanthochymol (monitored by TLC) were combined
and the solvent distilled off. The residue (7.5 g) crystallised from pet.ether (60-80°) in yellow needles m.p. 135° (Found: C, 75.8; H, 8.4. $C_{38}H_{50}O_6$ requires C, 75.8; H, 8.3%).

**Hydrogenation of xanthochymol**

Xanthochymol (0.5 g) was hydrogenated using 5% palladised charcoal (0.2 g) in ethyl acetate (100 ml) at 80 psi for 8 hr. Filtered to remove the catalyst and the solvent distilled off. The residue (0.5 g) was chromatographed on a column of silica gel using pet.ether (60-80°)/acetone as the eluent with increasing polarity. The fractions containing the faster moving octahydroxanthochymol (monitored by TLC) were combined and the solvent was distilled off. Residue (0.12 g) had no tendency to crystallised ($M^+ 610$; Found: C, 74.8; H, 7.5. $C_{38}H_{58}O_6$ requires C, 74.7; H, 7.5%). Latter fractions containing the slower moving tetrahydroxanthochymol were combined and the solvent distilled off. The residue (0.26 g) crystallised from pet.ether (60-80°) in yellow needles, m.p. 171-73° ($M^+ 606$, Found: C, 75.1; H, 9.0. $C_{38}H_{54}O_6$ requires C, 75.2; H, 8.9%).

**Methylene xanthochymol**

Xanthochymol (0.1 g), anhydrous potassium carbonate (3 g), dry acetone (30 ml) and methylene iodide
(2 ml) were refluxed for 18 hr. The solvent distilled off, cooled and added water. Extracted with ether (2 x 25 ml), washed with the ether layer with water; dried over anhydrous sodium sulphate, filtered and evaporated the solvent.

Preparative TLC of the residue (0.1 g) on silica gel using 20% acetone in pet. ether (60-80°) as the developing solvent gave methylene derivative (0.04 g) which had no tendency to crystallise (M+ 614; Found: C, 76.2; H, 8.0. C39H50O6 requires C, 76.2; H, 8.1%).

**Xanthochymol carbonate**

Xanthochymol (0.1 g) was dissolved in sodium hydroxide solution (0.2 g of sodium hydroxide was dissolved in 15 ml of deaerated water). Cooled to 0° and bubbled nitrogen for 5 minutes. Added phosgene in toluene (20%; 2 ml) and stirred for 1 hr. Again bubbled nitrogen to remove excess of phosgene. Acidified and extracted with ether. The product (0.1 g) was purified by preparative TLC on silica gel using 20% acetone in pet. ether as the developing solvent. The carbonate (0.06 g) resisted crystallisation. (IR: –O–CO– carbonyl, 1840 cm⁻¹; six-membered ring – CO, 1720; ArCO, 1650 cm⁻¹).

**Xanthochymol trimethyl ether**

(a) Xanthochymol (0.2 g) was dissolved in ether (20 ml) and added etherial diazomethane (50 ml) and kept in the refrigerator for 24 hr. The product showed two distinct spots on alumina TLC (solvent: benzene).
(b) Xanthochymol (0.2 g), anhydrous potassium carbonate (3 g), dry acetone (30 ml), and dimethyl sulphate (1 ml) were refluxed for 6 hr. Extracted the product with ether (2 x 50 ml) and evaporated the solvent. The residue (0.2 g) showed similar chromatographic behaviour as in the above experiment.

**Separation of the two methyl ethers**

The product in the above experiments (0.4 g) was chromatographed on a column of neutral alumina which was previously deactivated by soaking in ethyl acetate for 24 hr. Benzene was used as the eluent. Earlier fractions containing xanthochymol trimethyl ether A were pooled and the solvent was evaporated. The residue (0.12 g) resisted crystallisation ($M^+$ 644; Found: C, 76.0; H, 8.8. $C_{41}H_{56}O_6$ requires C, 76.4; H, 8.7%).

The latter fractions containing xanthochymol trimethyl ether B were pooled and the solvent was evaporated. The residue (0.20 g) resisted crystallisation ($M^+$ 644. Found: C, 76.1; H, 8.8. $C_{41}H_{56}O_6$ requires C, 76.4; H, 8.7%).

**Xanthochymol dimethyl ether**

A mixture of trimethyl ethers of xanthochymol (0.4 g) was dissolved in 5% ethanolic sodium hydroxide (20 ml) and refluxed for 9 hr. Concentrated to small volume
under reduced pressure and diluted with water (50 ml).
Extracted with ether (3 x 50 ml); washed with aqueous
sodium bicarbonate; dried on anhydrous sodium sulphate
and the solvent was evaporated. The residue (0.38 g)
on preparative layer chromatography (silica gel; pet.ether/
acetone, 3:1) gave xanthochymol dimethyl ether (0.164 g),
which resisted crystallisation. (M$^+$ 630; Found: C, 76.1; H, 8.7.
C$_{40}$H$_{54}$O$_6$ requires C, 76.2; H, 8.5%).

Remethylation of xanthochymol dimethyl ether

Xanthochymol dimethyl ether (0.025 g) was dissolved
in methanol (2 ml), cooled to 0°, added ethereal diazomethane
(10 ml) and kept in the refrigerator for 24 hr. The product
(0.025 g) had no tendency to crystallise. It showed single
spot on silica gel TLC (acetone–pet.ether 2:8), but two spots on alumina TLC (solvent: benzene).

Methylation of octahydroxanthochymol

Octahydroxanthochymol (0.1 g) was dissolved in
methanol (3 ml), cooled to 0°, added ethereal diazomethane
(30 ml) and kept in the refrigerator for 12 hr.

Chromatography of the product on a column of neutral alumina using benzene/pet.ether (1:1) as the eluent
gave the faster moving octahydroxanthochymol trimethyl ether A (0.04 g) which resisted crystallisation (M$^+$ 652.
Found: C, 75.6; H, 9.9. C$_{41}$H$_{64}$O$_6$ requires C, 75.4; H, 9.8%).
The slower moving octahydroxanthochyraol trimethyl ether B (0.045 g) also resisted crystallisation ($M^+ 652$. Found: C, 75.5; H, 9.9. $C_{41}H_{64}O_6$ requires C, 75.4; H, 9.8%).

**Xanthochymol di-(p-bromobenzene) sulphonate**

Xanthochymol (0.25 g), anhydrous potassium carbonate (3 g), dry acetone (25 ml) and p-bromobenzene sulphonyl chloride (0.3 g) were refluxed on water bath for 40 hr. The product was purified on a column of silica gel using acetone/pet.ether as the eluent with increasing polarity. Crystallised xanthochymol di(p-bromobenzene) sulphonate (0.3 g) from methanol in colourless needles, m.p. 120° (Found: C, 57.5; H, 5.2; S, 6.0; Br, 15.0. $C_{50}H_{56}O_{10}S_2Br_2$ requires C, 57.7; H, 5.3; S, 6.1; Br, 15.3%).

**Methylation of xanthochymol di(p-bromobenzene) sulphonate**

Xanthochymol di(p-bromobenzene) sulphonate (0.2 g), anhydrous potassium carbonate (3 g), dry acetone (30 ml) and dimethyl sulphate (2 ml) were refluxed for 4 hr. The product (0.2 g) crystallised from methanol in colourless needles (m.p. 65°) but showed two spots on alumina TLC, (benzene-pet.ether 1:1).

**Isolation of isoxanthochymol (IV)**

Petroleum ether extract (30 g) of the fruits of *G. xanthochymus* was chromatographed on a column of silica gel (500 g) using pet.ether (60-80°)/acetone as the eluent. After eluting the oil (may be a terpenoid) (5 g) and
and xanthochymol (7.5 g), the fractions containing iso-
xanthochymol (fractions were examined by TLC) were
combined and the solvent was distilled off. Crystallised
the residue (2 g) from pet.ether/acetone in pale yellow
needles, m.p. 222° (M⁺ 602. Found: C, 75.7; H, 8.0.
C₃₈H₅₄O₆ requires C, 75.7; H, 8.3%).

Hydrogenation of isoxanthochymol

Isoxanthochymol (0.1 g) was hydrogenated in
ethanol (25 ml) using 10% palladised charcoal (0.03 g)
as the catalyst. When ceased to absorb any more of the
hydrogen filtered to remove the catalyst. Crystallised
the product (0.11 g) from pet.ether/acetone in colourless
needles, m.p. 188° (M⁺ 608. Found: C, 75.1; H, 9.7.
C₃₈H₅₄O₆ requires C, 75.0; H, 9.2%).

Isoxanthochymol dimethyl ether

A mixture of isoxanthochymol (0.15 g), anhydrous
potassium carbonate (3 g), dimethyl sulphate (1 ml) and
dry acetone (30 ml) was refluxed for 15hr. Extracted the
product with ethyl acetate. The dimethyl ether (0.16 g)
had no tendency to crystallise (M⁺ 630. Found: C, 76.3;
H, 8.6. C₄₀H₅₄O₆ requires C, 76.1; H, 8.5%).

Hexahydroisoxanthochymol dimethyl ether

A mixture of hexahydroisoxanthochymol (0.13 g),
anhydrous potassium carbonate (3 g), dimethyl sulphate(1 ml)
and dry acetone (30 ml) was refluxed for 12 hr. Work up of the product and chromatography on a column of silica gel (eluent; benzene) gave hexahydroisoxanthochymol dimethyl ether (0.16 g), which was crystallised from pet.ether in colourless needles, m.p. 170° (M* 636. Found: C, 75.3; H, 9.2. C₄₀H₆₀O₆ requires C, 75.4; H, 9.4%).

**Oxidation of hexahydroisoxanthochymol with DDQ**

Hexahydroisoxanthochymol (0.12 g), dichlorodicyanobenzoquinone (0.12 g) and dry benzene (30 ml) were refluxed for 12 hr. Cooled, filtered, and washed the residue with benzene. The solvent was evaporated and the residue (0.15 g) was chromatographed on a column of silica gel using benzene as the eluent. Fractions containing the faster moving yellow compound were combined and the solvent was distilled off. The product (0.03 g), crystallised from pet.ether in orange needles, m.p. 186° (λ_max. 230, 254.5; 275 and 432 nm.)

**Ozonolysis of isoxanthochymol dimethyl ether**

Isoxanthochymol dimethyl ether (0.5 g) was dissolved in ethylacetate (20 ml), cooled to 0° and passed ozone (0.12 g). The solvent was removed under reduced pressure, dissolved the ozonide in acetone (20 ml), cooled to 0°, added Jones reagent dropwise till purple colour persisted (2 ml). Stirred for 15 minutes. Acetone
was removed under reduced pressure and diluted with water (100 ml). Extracted with ethylacetate. The ethylacetate layer was then extracted with 5% sodium bicarbonate aqueous (2 x 25 ml) and acidified the extract. The acidic compound thus obtained was esterified with diazomethane. The ester (V) was purified by chromatography (silica gel, acetone/pet.ether, 2:8), which showed no tendency to crystallise ($M^+ 642$. Found: C, 63.2; H, 6.3. $C_{34}H_{42}O_{12}$ requires C, 63.5; H, 6.5%).

In another experiment hydrogenated the ozonide (0.2 g) in ethyl acetate (30 ml) using 5% palladised charcoal (0.1 g) as the catalyst. Filtered off the catalyst and distilled the filtrate. Collected the distillate in 2,4-dinitrophenylhydrazine solution. The mixture was kept in the refrigerator for 6 hr. Filtered off the deep red needles of 2,4-dinitrophenylhydrazone of acetone, m.p. 124-25°, lit. 29 m.p. 128°.

**Isoxanthochymol di-o-bromobenzene sulphonate**

Isoxanthochymol (0.25 g), anhydrous potassium carbonate (3 g), dry acetone (30 ml) and p-bromobenzene sulphonyl chloride (0.3 g) were refluxed for 40 hr. Work up of the product and chromatography (silica gel, acetone/pet.ether, 2:8) gave the dibrosylate, which was crystallised from methanol by equilibration in colourless long prisms (0.3 g), m.p. 100° (Found: C, 57.7; H, 5.2; S, 6.0; Br, 15.1. $C_{50}H_{56}O_{11}S_2Br_2$ requires C, 57.7; H, 5.3; S, 6.1; Br, 15.3%).
REFERENCES


21. Idem, ibid. 64 (1942), 72.


