Microanalyses were done in Alfred Bernhardt's Laboratory, W. Germany.


CHEMICAL COMPONENTS OF THE STEM BARK OF CEDRUS DEODARA: ISOLATION OF A NEW DIHYDROFLAVONOL

In an earlier publication1 was reported the isolation of 'deodarin' from the ether extract of the stem bark and it was assigned the tentative structure of 3', 4', 5, 6-tetrahydroxy-8-C-methyldihydroflavonol. It was considered to be individual based on paper chromatography. A careful re-examination of this product using TLC in various solvent systems and polyamide and silica gel column chromatography has led its resolution into two components, compounds A and B, almost is equal quantities.

Compound A had the molecular formula C15H12O7, m.p. 239-41°C, [α]D + 12° (MeOH). Its colour reactions indicated it to be a dihydroflavonol. It formed a tetramethyl ether, m.p. 169-70°C and a penta-acetate, m.p. 120°C. The physical and spectral properties of compound A and of its derivatives led to its identification as taxifolin and this was confirmed by direct comparison of its methyl ether with an authentic sample.

Compound B had the molecular formula C16H14O7, m.p. 226-27°C, [α]D + 19° (MeOH). It gave colour reactions characteristic of a dihydroflavonol. Its U.V. spectra with and without reagents were comparable with those of taxifolin. λmaxOH 293 (4.33) and 331 (inf) nm. It formed a tetramethyl ether, m.p. 214-15°C, whose NMR spectrum in CDCl3 resembled that of taxifolin tetramethyl ether but had a three proton singlet at 6 2.08 for an aromatic C-CH3 group and one-proton singlet at 6 6-30 belonging to A ring. The mass spectrum of the methyl ether confirmed the presence of a C-CH3 group in the A ring (m/e: 374 (M+), 207 and 195 (100%). Compound B formed a penta-acetate, m.p. 145°C, whose NMR spectrum in CDCl3 again confirmed the presence of a C-CH3 group in the A ring. The location of the C-methyl group in the 8-position has been determined by dehydrogenation with I2/KOAc in glacial acetic acid3 whereby a C-methyl flavon C16H13O7, m.p. 290-95°C was obtained. It differed from pinoquercitin (6-methyl quercetin)3. Its pentamethyl ether C21H22O7 (M+ 386), m.p. 220-21°C was identical with synthetic 8-C-methyl quercetin pentamethyl ether4 in all respects (m.m.p., TLC and IR). C-Methyl dihydroflavonols are rare; only quite recently 6-C-methyltaxifolin was reported to occur in Populus deltoides.5

Two more compounds, C and D were obtained from the polyamide column. Compound C, m.p. > 300°C, was found to be a flavonol and was identified as quercetin. Compound D was difficult to separate from compound C. It was also a flavonol comparing with 8-C-methyl quercetin on TLC. That these two compounds are not artefacts was proved by the fact that a fresh extract showed their presence on TLC examination.

Consequent on the above findings, the name 'deodarin' may now be applied to 8-C-methyl 3', 4', 5, 7-tetrahydroxy dihydroflavonol.

Our thanks are due to Prof. K. Venkataraman for a sample of pinoquercitin and the Council of Scientific and Industrial Research for a Research Fellowship to K. R.

Dept. of Chemistry, K. RAGHUNATHAN, Delhi University, S. RANGASWAMI, Delhi-7, July 22, 1971. T. R. SESHADEVI.


SYNTHESIS OF PIPERAZINE ETHANOL ACRYLATES AS POSSIBLE ANTIPHLOGISTICS AND ANALGESICS

Recent investigations by Elde Cresczenzi and others have shown that asymmetrical aryl piperazines mono acrylates are good anti-inflammatory compounds with analgesic and anti-pyretic activities. Some of them are anti-spasmodics also. In analgesics, especially, in the pyrrolidine group, it has been shown that the potency is very much enhanced if the nitrogen is substituted by the phenyl ethyl grouping.2 In general, many of the ring-sub-
stituted cinnamic acids and esters have shown anti-inflammatory properties. A survey of literature has revealed that an introduction of a phenyl ethyl grouping on the nitrogen of the present work, an attempt was made to synthesize a few of the compounds having the basic skeleton (I) incorporating the above features, where R is OCH₃; NO₂; Cl; etc.

![Chemical Structure](image)

**Table I**

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>M.P.</th>
<th>Theory N%</th>
<th>Found N%</th>
<th>Analgesic</th>
<th>Antinflammatory</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CH₃O</td>
<td>H</td>
<td>213-15 (d)</td>
<td>5.2</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(2) O₂N</td>
<td>H</td>
<td>255-58 (d)</td>
<td>8.7</td>
<td>8.3</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>(3) Cl</td>
<td>H</td>
<td>225-30 (d)</td>
<td>5.9</td>
<td>5.8</td>
<td>±</td>
<td>-</td>
</tr>
<tr>
<td>(4) CH₃O</td>
<td>H</td>
<td>225-30 (d)</td>
<td>6.0</td>
<td>6.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(5) Cl</td>
<td>H</td>
<td>232-35 (d)</td>
<td>5.9</td>
<td>5.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(6) OCH₂</td>
<td>H</td>
<td>182-185</td>
<td>6.0</td>
<td>6.5</td>
<td>±</td>
<td>-</td>
</tr>
<tr>
<td>(7)</td>
<td>H</td>
<td>228-31 (d)</td>
<td>6.5</td>
<td>6.7</td>
<td>±</td>
<td>-</td>
</tr>
<tr>
<td>(8)</td>
<td>H</td>
<td>240-43 (d)</td>
<td>6.3</td>
<td>6.3</td>
<td>±</td>
<td>-</td>
</tr>
<tr>
<td>(9) CH₃O</td>
<td>H</td>
<td>210-213 (d)</td>
<td>5.2</td>
<td>5.0</td>
<td>+</td>
<td>±</td>
</tr>
<tr>
<td>(10)</td>
<td></td>
<td>227-230</td>
<td>5.6</td>
<td>5.4</td>
<td>..</td>
<td>..</td>
</tr>
</tbody>
</table>

(+ ) Means equal to aspirin; (- ) No activity; (±) Nearly equal to aspirin.

Piperazine ethanol moiety followed by the esterification with the substituted cinnamic acids have not been synthesized and examined for their pharmacological properties. In the cinnamic acid part, the phenyl group has also been replaced with furan and thio-phenone ring systems. The possible use of bis-phenyl ethyl piperazines as anthelmintic
A NOTE ON THE ORDOVICIAN FOSSILS FROM THE BARAMULA DISTRICT, KASHMIR

The object of the present note is to place on record the occurrence of a few articulate brachiopods from the Ordovician rocks exposed near Marhaun (34° 34' ; 34° 10') in the Hundwa basin of Baramula District, Kashmir. These are in addition to the forms already described.1-3

During the course of recent investigations, the author made a huge collection of fossils, cut of which the following forms have for the present been identified:

Orthis (Eridolithis) cf. kalavensis Reed.
Orthis (Dalmanella) cf. emancipata Reed.
Orthis ? sp.
Leptelloidea cf. leptelloides (Bekker).
Leptochaena sp.
Leptochaena rhomboidalis Wilck.
Sowerbyella wilsoni Reed.
Rafinesquina sp.
Sphonomena sp. Resserella sp.
Ahtiella ? sp. Raymondella sp.

The presence of the species of Resserella and Raymondella with European affinities is important from stratigraphical point of view in that it will help in demarcating the boundary between Upper Ordovician and Lower to Middle Ordovician.

Resserella sp. in the present collection is affined to Resserella (Howellites) striata Bancroft recorded by Bancroft1 from the Upper Ordovician rocks of Europe. Raymondella sp. has also close similarities to Raymondella type Bancroft of the Upper Ordovician horizons of Europe. Rest of the forms, listed above, are long-ranging and occur throughout the Ordovician rocks in the present area.

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in Geology,
Panjab University,
Chandigarh-14, April 16, 1971.

1. Wadia, D. N., "The Cambrian-Trias sequence of North-Western Kashmir (Parts of Muzaffarabad and Baramula Districts)," Rec. Geol. Surv. Ind., 1934, 68.

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