THE REFRACTIVE DISPERSIVE POWER OF ORGANIC COMPOUNDS

Part II. The Camphor-β-sulphonates (d- and dl-) of o-, m-, p-
Toluidines, o-, m-, p-Iodanilines, α-Amino-pyridine,
α-Aminothiazole, p-Aminobenzensulphonamide
and 6-Methoxy-8-aminooquinoline

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In Part I of this series of investigations,1 the refractive dispersion of dextro,
lævo and racemic forms of several terpene derivatives was described. It was
pointed out that the earlier formulæ of Gladstone and Dale2 \( \left( \frac{n^2 - 1}{d} \right) \) and
of Lorenz and Lorentz,3 \( \frac{n^2 - 1}{(n^2 + 1)d} \) for refractive power were defective as
they do not take into account the effects of dispersion. This difficulty was
removed by the work of Maxwell and Sellmeier4 who proposed the dispersion
formula as

\[ n^2 = a^2 + \sum \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}. \]  

(i)

It is found that generally one term of the summation in this equation when
added to a constant \( a^2 \) is sufficient to represent correctly the refractive disper-
sive power of different types of organic compounds of varying complexity.

In this paper we record the results of our experiments on the refractive
dispersion of the camphor-β-sulphonates (d- and dl-) of eleven aromatic and
heterocyclic primary amines in aqueous solution (Tables II–XII). The refractive dispersion of these salts can be satisfactorily expressed by the
Maxwell-Sellmeier simplified expression,

\[ n^2 = a^2 + \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}, \]  

(ii)
in which \( b_0 \) is the refraction constant and \( \lambda_0^2 \) the dispersion constant. The
constant term \( a^2 \), when added to one term of the summation in equation (i),
namely, \( \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2} \) gives the square of the refractive index of the medium for
a stationary electric field. The values of \( \lambda_0 s \)—the wavelengths of the

140
| No. | Compound | \([\alpha]_{\text{abs}} = \lambda_0\)  
(Drude Equation for \(\lambda = \sqrt{1+\lambda_0^2}\)) | \([\sigma]_{\text{abs}} = \sqrt{\frac{\lambda_0^2}{\lambda^2 + \lambda_0^2}}\)  
(Maxwell-Sellmeier Equation for \(\lambda = \sqrt{1+\lambda_0^2}\)) | \(\lambda_0\)  
(From Drude Equation) | \(\lambda_0\)  
(Maxwell-Sellmeier Equation) | \(\lambda_0\)  
(Mean value of columns 5 and 6) | \(\lambda_0\)  
(Difference of columns 5 and 6) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>(\dagger) R·SO₂H·H₂N&lt;br&gt;CH₂</td>
<td>3.400</td>
<td>1.3301</td>
<td>3606</td>
<td>3620</td>
<td>3613</td>
<td>-14</td>
</tr>
<tr>
<td>2a</td>
<td>R·SO₃H·H₂N&lt;br&gt;CH₃</td>
<td>3.367</td>
<td>1.3284</td>
<td>3562</td>
<td>3540</td>
<td>3551</td>
<td>+22</td>
</tr>
<tr>
<td>3a</td>
<td>R·SO₂H·H₂N&lt;br&gt;CH₃</td>
<td>3.310</td>
<td>1.3285</td>
<td>3536</td>
<td>3533</td>
<td>3534</td>
<td>+3</td>
</tr>
<tr>
<td>4a</td>
<td>R·SO₂H·H₂N&lt;br&gt;CH₃</td>
<td>3.300</td>
<td>1.3289</td>
<td>3597</td>
<td>3571</td>
<td>3584</td>
<td>+26</td>
</tr>
<tr>
<td>5b</td>
<td>Rs·SO₃H·H₂N&lt;br&gt;CH₂</td>
<td>3.110</td>
<td>1.3316</td>
<td>3669</td>
<td>3659</td>
<td>3664</td>
<td>+10</td>
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<tr>
<td>6b</td>
<td>R·SO₂H·H₂N&lt;br&gt;CH₂</td>
<td>3.288</td>
<td>1.3319</td>
<td>3664</td>
<td>3667</td>
<td>3666</td>
<td>-3</td>
</tr>
<tr>
<td>7b</td>
<td>R·SO₂H·H₂N&lt;br&gt;CH₂</td>
<td>3.207</td>
<td>1.3319</td>
<td>3658</td>
<td>3637</td>
<td>3647</td>
<td>+21</td>
</tr>
<tr>
<td>8b</td>
<td>R·SO₂H·H₂N&lt;br&gt;CH₂</td>
<td>3.307</td>
<td>1.3292</td>
<td>3289</td>
<td>3292</td>
<td>3290</td>
<td>-3</td>
</tr>
<tr>
<td>9c</td>
<td>R·SO₂H·H₂N&lt;br&gt;CH₂</td>
<td>4.155</td>
<td>1.3297</td>
<td>3537</td>
<td>3544</td>
<td>3540</td>
<td>-7</td>
</tr>
<tr>
<td>10d</td>
<td>R·SO₂H·H₂N&lt;br&gt;SO₂NH₂&lt;br&gt;CH₃O</td>
<td>2.793</td>
<td>1.3301</td>
<td>3668</td>
<td>3676</td>
<td>3672</td>
<td>-8</td>
</tr>
<tr>
<td>11c</td>
<td>R·SO₂H·H₂N&lt;br&gt;CH₂</td>
<td>3.294</td>
<td>1.3290</td>
<td>3131</td>
<td>3172</td>
<td>3151</td>
<td>-41</td>
</tr>
</tbody>
</table>

\(\dagger\) R = C₁₀H₁₅O or \[
\begin{align*}
\text{CH₂} & - \\
\text{CH₃} & - \\
\text{C} & - \\
\text{CH₃} & - \\
\text{CH₂} & - \\
\end{align*}
\]

The abbreviation for which R stands is the same in all the Tables I to XII.


TABLE II
Refractive Dispersion of Anilinocamphor-β-sulphonates

\[
\begin{align*}
R \cdot SO_3H \cdot H_2N- & \\
\frac{\eta^2}{\lambda^2} = 1.7578 + \frac{0.01121 \lambda^2}{\lambda^2 - 1.311}; & \quad \lambda^2 = 0.13111 \\
\frac{\eta^2}{\lambda^2} = 1.7578 + \frac{0.01121 \lambda^2}{\lambda^2 - 1.311}; & \quad \lambda^2 = 0.3606 \\
[a]^* = \frac{3.400}{\lambda^2 - 0.1300}; & \quad \lambda^2 = 0.1300 \\
[a]^* = \frac{3.400}{\lambda^2 - 0.1300}; & \quad \lambda^2 = 0.3620 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(\eta_{\text{calculated}})</th>
<th>(\eta_{\text{d-ε}})</th>
<th>(\eta_{\text{r-ε}})</th>
<th>(\eta_{\text{d-r}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_6708</td>
<td>1.3314</td>
<td>1.3317</td>
<td>+0.0003</td>
<td>1.3316</td>
</tr>
<tr>
<td>Na_5803</td>
<td>1.3322</td>
<td>1.3324</td>
<td>+0.0002</td>
<td>1.3321</td>
</tr>
<tr>
<td>Hg_5270</td>
<td>1.3324</td>
<td>1.3324</td>
<td>±0.0000</td>
<td>1.3324</td>
</tr>
<tr>
<td>Hg_5461</td>
<td>1.3330</td>
<td>1.3331</td>
<td>+0.0001</td>
<td>1.3330</td>
</tr>
<tr>
<td>Hg_4638</td>
<td>1.3380</td>
<td>1.3380</td>
<td>-0.0001</td>
<td>1.3380</td>
</tr>
</tbody>
</table>

* The rotatory dispersion equation is taken from Singh, Pertin and Singh, Proc. Lahore Phil. Soc., 1944, 6, 15; Allahabad University Studies, 1944, 37, 57.

TABLE III
Refractive Dispersion of o-Toluidinocamphor-β-sulphonates

\[
\begin{align*}
R \cdot SO_3H \cdot H_2N- & \\
\frac{\eta^2}{\lambda^2} = 1.7506 + \frac{0.01582 \lambda^2}{\lambda^2 - 1.253}; & \quad \lambda^2 = 0.12531 \\
\frac{\eta^2}{\lambda^2} = 1.7506 + \frac{0.01582 \lambda^2}{\lambda^2 - 1.253}; & \quad \lambda^2 = 0.3582 \\
[a]^* = \frac{3.367}{\lambda^2 - 0.1269}; & \quad \lambda^2 = 0.1269 \\
[a]^* = \frac{3.367}{\lambda^2 - 0.1269}; & \quad \lambda^2 = 0.3540 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(\eta_{\text{calculated}})</th>
<th>(\eta_{\text{d-ε}})</th>
<th>(\eta_{\text{r-ε}})</th>
<th>(\eta_{\text{d-r}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_6708</td>
<td>1.3300</td>
<td>1.3297</td>
<td>-0.0003</td>
<td>1.3301</td>
</tr>
<tr>
<td>Na_5803</td>
<td>1.3306</td>
<td>1.3309</td>
<td>+0.0003</td>
<td>1.3304</td>
</tr>
<tr>
<td>Hg_5270</td>
<td>1.3311</td>
<td>1.3311</td>
<td>±0.0000</td>
<td>1.3310</td>
</tr>
<tr>
<td>Hg_5461</td>
<td>1.3317</td>
<td>1.3320</td>
<td>+0.0003</td>
<td>1.3314</td>
</tr>
<tr>
<td>Hg_4638</td>
<td>1.3378</td>
<td>1.3377</td>
<td>-0.0001</td>
<td>1.3378</td>
</tr>
</tbody>
</table>

### Table IV

**Refractive Dispersion of m-Toluidinocamphor-β-sulphonates**

\[
\{ \begin{align*}
\eta^2 &= 1.7511 + \frac{0.01325\lambda^2}{\lambda^2 - 0.1249}; \\
[\alpha] &= \frac{3.31}{\lambda^2 - 0.1250}; \\
\lambda_0 &= 0.3535; \\
\lambda_0^2 &= 0.1250; \\
\lambda_0 &= 0.3535; \\
\lambda_0^2 &= 0.1250.
\end{align*} \]

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>( \eta^2 )</th>
<th>( \eta_d )</th>
<th>( \eta_r )</th>
<th>( \eta_{d-r} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li 6708</td>
<td>1.3302</td>
<td>1.3304</td>
<td>1.3304</td>
<td>±0.0000</td>
</tr>
<tr>
<td>Na 5898</td>
<td>1.3311</td>
<td>1.3310</td>
<td>1.3312</td>
<td>±0.0001</td>
</tr>
<tr>
<td>Hg 5760</td>
<td>1.3313</td>
<td>1.3313</td>
<td>1.3314</td>
<td>±0.0001</td>
</tr>
<tr>
<td>Hg 5461</td>
<td>1.3319</td>
<td>1.3320</td>
<td>1.3320</td>
<td>±0.0001</td>
</tr>
<tr>
<td>Hg 43558</td>
<td>1.3378</td>
<td>1.3378</td>
<td>1.3374</td>
<td>±0.0004</td>
</tr>
</tbody>
</table>


### Table V

**Refractive Dispersion of p-Toluidinocamphor-β-sulphonates**

\[
\{ \begin{align*}
\eta^2 &= 1.7520 + \frac{0.01247\lambda^2}{\lambda^2 - 0.1276}; \\
[\alpha] &= \frac{3.39}{\lambda^2 - 0.1294}; \\
\lambda_0 &= 0.3597; \\
\lambda_0^2 &= 0.1294; \\
\lambda_0 &= 0.3597; \\
\lambda_0^2 &= 0.1294.
\end{align*} \]

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>( \eta^2 )</th>
<th>( \eta_d )</th>
<th>( \eta_r )</th>
<th>( \eta_{d-r} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li 4708</td>
<td>1.3302</td>
<td>1.3303</td>
<td>1.3302</td>
<td>±0.0000</td>
</tr>
<tr>
<td>Na 5898</td>
<td>1.3310</td>
<td>1.3309</td>
<td>1.3311</td>
<td>±0.0000</td>
</tr>
<tr>
<td>Hg 5760</td>
<td>1.3311</td>
<td>1.3311</td>
<td>1.3312</td>
<td>±0.0000</td>
</tr>
<tr>
<td>Hg 5461</td>
<td>1.3318</td>
<td>1.3318</td>
<td>1.3316</td>
<td>±0.0000</td>
</tr>
<tr>
<td>Hg 43558</td>
<td>1.3379</td>
<td>1.3379</td>
<td>1.3380</td>
<td>±0.0001</td>
</tr>
</tbody>
</table>

**TABLE VI**

Refractive Dispersion of o-Iodanilinocamphor-β-sulphonates

\[
\begin{align*}
R\cdot SO_2H\cdot H_2N- & \quad \text{I} \\
\left\{
\begin{array}{ll}
\lambda^2 &= 1.7632 + \frac{0.00685\lambda^2}{\lambda^2 - 0.1339} \\
\alpha^2 &= 1.7632 + \frac{0.00685\lambda^2}{\lambda^2 - 0.1345}
\end{array}
\right.
\end{align*}
\]

\[
\left\{ [\alpha]^{*} = \frac{3.11}{\lambda^2 - 0.1346} \quad \lambda_0^2 = 0.1339 \quad \lambda_0 = 0.3669 \\
[\alpha]^{*} = \frac{3.268}{\lambda^2 - 0.1342} \quad \lambda_0^2 = 0.1345 \quad \lambda_0 = 0.3664
\right.
\]

<table>
<thead>
<tr>
<th>λ</th>
<th>Calculated (ε)</th>
<th>Dextro (d)</th>
<th>d−ε</th>
<th>Racemic (r)</th>
<th>r−ε</th>
<th>d−r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li&lt;sub&gt;2+&lt;/sub&gt;</td>
<td>1.3325</td>
<td>1.3328</td>
<td>+0.0003</td>
<td>1.3324</td>
<td>−0.0001</td>
<td>+0.0004</td>
</tr>
<tr>
<td>Na&lt;sub&gt;5+&lt;/sub&gt;</td>
<td>1.3331</td>
<td>1.3330</td>
<td>−0.0001</td>
<td>1.3330</td>
<td>−0.0001</td>
<td>±0.0000</td>
</tr>
<tr>
<td>Hg&lt;sub&gt;5+5&lt;/sub&gt;</td>
<td>1.3332</td>
<td>1.3331</td>
<td>−0.0001</td>
<td>1.3333</td>
<td>+0.0001</td>
<td>−0.0002</td>
</tr>
<tr>
<td>Hg&lt;sub&gt;9+&lt;/sub&gt;</td>
<td>1.3337</td>
<td>1.3335</td>
<td>−0.0002</td>
<td>1.3340</td>
<td>+0.0003</td>
<td>−0.0005</td>
</tr>
<tr>
<td>Hg&lt;sub&gt;15+&lt;/sub&gt;</td>
<td>1.3338</td>
<td>1.3339</td>
<td>+0.0002</td>
<td>1.3339</td>
<td>+0.0001</td>
<td>+0.0001</td>
</tr>
</tbody>
</table>


**TABLE VII**

Refractive Dispersion of m-Iodanilinocamphor-β-sulphonates

\[
\begin{align*}
R\cdot SO_2H\cdot H_2N- & \quad \text{I} \\
\left\{
\begin{array}{ll}
\lambda^2 &= 1.7643 + \frac{0.008138\lambda^2}{\lambda^2 - 0.1345} \\
\alpha^2 &= 1.7643 + \frac{0.008138\lambda^2}{\lambda^2 - 0.1345}
\end{array}
\right.
\end{align*}
\]

\[
\left\{ [\alpha]^{*} = \frac{3.268}{\lambda^2 - 0.1342} \quad \lambda_0^2 = 0.1345 \quad \lambda_0 = 0.3664 \\
[\alpha]^{*} = \frac{3.268}{\lambda^2 - 0.1342} \quad \lambda_0^2 = 0.1345 \quad \lambda_0 = 0.3664
\right.
\]

<table>
<thead>
<tr>
<th>λ</th>
<th>Calculated (ε)</th>
<th>Dextro (d)</th>
<th>d−ε</th>
<th>Racemic (r)</th>
<th>r−ε</th>
<th>d−r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li&lt;sub&gt;2+&lt;/sub&gt;</td>
<td>1.3328</td>
<td>1.3328</td>
<td>±0.0000</td>
<td>1.3327</td>
<td>−0.0001</td>
<td>+0.0001</td>
</tr>
<tr>
<td>Na&lt;sub&gt;5+&lt;/sub&gt;</td>
<td>1.3335</td>
<td>1.3334</td>
<td>−0.0001</td>
<td>1.3332</td>
<td>−0.0003</td>
<td>+0.0001</td>
</tr>
<tr>
<td>Hg&lt;sub&gt;5+5&lt;/sub&gt;</td>
<td>1.3336</td>
<td>1.3337</td>
<td>+0.0001</td>
<td>1.3334</td>
<td>−0.0003</td>
<td>+0.0002</td>
</tr>
<tr>
<td>Hg&lt;sub&gt;9+&lt;/sub&gt;</td>
<td>1.3340</td>
<td>1.3338</td>
<td>−0.0002</td>
<td>1.3341</td>
<td>+0.0001</td>
<td>−0.0003</td>
</tr>
<tr>
<td>Hg&lt;sub&gt;15+&lt;/sub&gt;</td>
<td>1.3339</td>
<td>1.3338</td>
<td>−0.0001</td>
<td>1.3339</td>
<td>+0.0001</td>
<td>−0.0002</td>
</tr>
</tbody>
</table>

### TABLE VIII

**Refractive Dispersion of p-Iodanilinocamphor-\(\beta\)-sulphonates**

\[ n^2 = 1.7644 + \frac{0.008404\lambda^2}{\lambda^2 - 0.1333}; \]

\[ \lambda_0^2 = 0.1333; \]

\[ \lambda_0 = 0.3658; \]

\[ \lambda_0^2 = 0.1338; \]

\[ \lambda_0 = 0.3637; \]

\[ [\alpha]^* = \frac{3.207}{\lambda^2 - 0.1338}; \]

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(n_{\text{Calculated}} )</th>
<th>(n_{\text{Dextro}} )</th>
<th>(n_{d-c} )</th>
<th>(n_{\text{Racemic}} )</th>
<th>(n_{r-c} )</th>
<th>(n_{d-r} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_{6708})</td>
<td>1.3328</td>
<td>1.3327</td>
<td>-0.0001</td>
<td>1.3328</td>
<td>±0.0000</td>
<td>-0.0001</td>
</tr>
<tr>
<td>Na(_{5683})</td>
<td>1.3334</td>
<td>1.3333</td>
<td>-0.0001</td>
<td>1.3335</td>
<td>+0.0001</td>
<td>-0.0002</td>
</tr>
<tr>
<td>Hg(_{5780})</td>
<td>1.3336</td>
<td>1.3338</td>
<td>+0.0002</td>
<td>1.3337</td>
<td>+0.0001</td>
<td>+0.0001</td>
</tr>
<tr>
<td>Hg(_{5461})</td>
<td>1.3340</td>
<td>1.3341</td>
<td>+0.0001</td>
<td>1.3339</td>
<td>-0.0001</td>
<td>+0.0002</td>
</tr>
<tr>
<td>Hg(_{4358})</td>
<td>1.3389</td>
<td>1.3390</td>
<td>+0.0001</td>
<td>1.3387</td>
<td>-0.0002</td>
<td>+0.0003</td>
</tr>
</tbody>
</table>


### TABLE IX

**Refractive Dispersion of \(\alpha\)-Aminopyridinocamphor-\(\beta\)-sulphonates**

\[ n^2 = 1.7432 + \frac{0.02134\lambda^2}{\lambda^2 - 0.1084}; \]

\[ \lambda_0^2 = 0.1084; \]

\[ \lambda_0 = 0.3289; \]

\[ \lambda_0^2 = 0.1082; \]

\[ \lambda_0 = 0.3292; \]

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(n_{\text{Calculated}} )</th>
<th>(n_{\text{Dextro}} )</th>
<th>(n_{d-c} )</th>
<th>(n_{\text{Racemic}} )</th>
<th>(n_{r-c} )</th>
<th>(n_{d-r} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_{6708})</td>
<td>1.3309</td>
<td>1.3310</td>
<td>+0.0001</td>
<td>1.3310</td>
<td>+0.0001</td>
<td>±0.0000</td>
</tr>
<tr>
<td>Na(_{5683})</td>
<td>1.3320</td>
<td>1.3321</td>
<td>+0.0001</td>
<td>1.3319</td>
<td>-0.0001</td>
<td>+0.0002</td>
</tr>
<tr>
<td>Hg(_{5780})</td>
<td>1.3321</td>
<td>1.3321</td>
<td>±0.0000</td>
<td>1.3322</td>
<td>+0.0001</td>
<td>-0.0001</td>
</tr>
<tr>
<td>Hg(_{5461})</td>
<td>1.3329</td>
<td>1.3328</td>
<td>-0.0001</td>
<td>1.3331</td>
<td>+0.0002</td>
<td>-0.0003</td>
</tr>
<tr>
<td>Hg(_{4358})</td>
<td>1.3390</td>
<td>1.3390</td>
<td>±0.0000</td>
<td>1.3389</td>
<td>-0.0001</td>
<td>+0.0001</td>
</tr>
</tbody>
</table>

### Table X

**Refractive Dispersion of α-Aminothiazolecamphor-β-sulphonates**

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$n^{\text{Calculated}}$</th>
<th>$n^{\text{Dextro}}$</th>
<th>$n_{d-c}$</th>
<th>$n^{\text{Racemic}}$</th>
<th>$n_{r-c}$</th>
<th>$n_{d-r}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3310</td>
<td>1.3312</td>
<td>+0.0002</td>
<td>1.3311</td>
<td>+0.0001</td>
<td>+0.0001</td>
<td></td>
</tr>
<tr>
<td>1.3319</td>
<td>1.3318</td>
<td>-0.0001</td>
<td>1.3320</td>
<td>+0.0001</td>
<td>-0.0002</td>
<td></td>
</tr>
<tr>
<td>1.3321</td>
<td>1.3321</td>
<td>±0.0000</td>
<td>1.3320</td>
<td>-0.0001</td>
<td>+0.0001</td>
<td></td>
</tr>
<tr>
<td>1.3327</td>
<td>1.3330</td>
<td>+0.0003</td>
<td>1.3329</td>
<td>+0.0002</td>
<td>+0.0001</td>
<td></td>
</tr>
<tr>
<td>1.3387</td>
<td>1.3387</td>
<td>±0.0000</td>
<td>1.3384</td>
<td>-0.0003</td>
<td>+0.0003</td>
<td></td>
</tr>
</tbody>
</table>


### Table XI

**Refractive Dispersion of p-Aminobenzene Sulphonamidocamphor-β-sulphonates**

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$n^{\text{Calculated}}$</th>
<th>$n^{\text{Dextro}}$</th>
<th>$n_{d-c}$</th>
<th>$n^{\text{Racemic}}$</th>
<th>$n_{r-c}$</th>
<th>$n_{d-r}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3312</td>
<td>1.3314</td>
<td>+0.0002</td>
<td>1.3314</td>
<td>+0.0002</td>
<td>±0.0000</td>
<td></td>
</tr>
<tr>
<td>1.3320</td>
<td>1.3321</td>
<td>+0.0001</td>
<td>1.3320</td>
<td>±0.0000</td>
<td>+0.0001</td>
<td></td>
</tr>
<tr>
<td>1.3321</td>
<td>1.3321</td>
<td>±0.0000</td>
<td>1.3322</td>
<td>+0.0001</td>
<td>-0.0001</td>
<td></td>
</tr>
<tr>
<td>1.3327</td>
<td>1.3329</td>
<td>+0.0002</td>
<td>1.3328</td>
<td>+0.0001</td>
<td>+0.0001</td>
<td></td>
</tr>
<tr>
<td>1.3389</td>
<td>1.3387</td>
<td>-0.0002</td>
<td>1.3387</td>
<td>-0.0002</td>
<td>±0.0000</td>
<td></td>
</tr>
</tbody>
</table>

### Table XII
Refractive Dispersion of 6-Methoxy-8-aminoquinolinocamphor-β-sulphonates

\[
\begin{align*}
\text{R} \cdot \text{SO}_3\text{H} \cdot \text{H}_2\text{N} & \quad \bigcirc \\
\lambda_0^2 & = 0.1006 \\
\lambda_0 & = 0.3131 \\
\lambda_0^2 & = 0.098 \\
\lambda_0 & = 0.3172 \\
[\alpha]^* & = \frac{3.294}{\lambda^2 - 0.3098} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>λ</th>
<th>(\pi_{\text{Calculated}}) ((\pi))</th>
<th>(\pi_{\text{Laevol}}) ((\pi))</th>
<th>(\pi_{\text{Laevol}}) ((\pi))</th>
<th>(\pi_{\text{Dextro}}) ((\pi))</th>
<th>(\pi_{\text{Dextro}}) ((\pi))</th>
<th>(\pi_{\text{Racemic}}) ((\pi))</th>
<th>(\pi_{\text{Racemic}}) ((\pi))</th>
<th>(\pi_{\text{Racemic}}) ((\pi))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₈₇₀₅</td>
<td>1.3312</td>
<td>± 0.0000</td>
<td>± 0.0000</td>
<td>1.3310</td>
<td>± 0.0002</td>
<td>1.3311</td>
<td>−0.0001</td>
<td></td>
</tr>
<tr>
<td>Na₃₈₈₃</td>
<td>1.3327</td>
<td>1.3328</td>
<td>+0.0001</td>
<td>1.3327</td>
<td>± 0.0000</td>
<td>1.3328</td>
<td>+0.0001</td>
<td></td>
</tr>
<tr>
<td>H₂₅₇₈₀</td>
<td>1.3329</td>
<td>1.3329</td>
<td>±0.0000</td>
<td>1.3329</td>
<td>±0.0000</td>
<td>1.3330</td>
<td>+0.0001</td>
<td></td>
</tr>
<tr>
<td>H₂₅₄₆₁</td>
<td>1.3338</td>
<td>1.3337</td>
<td>−0.0001</td>
<td>1.3338</td>
<td>±0.0000</td>
<td>1.3336</td>
<td>−0.0002</td>
<td></td>
</tr>
<tr>
<td>H₂₄₃₈₈</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td></td>
</tr>
</tbody>
</table>


“Characteristic” absorption bands—have been calculated from these equations and are compared with those derived from rotatory dispersion equations of Drude and are found to be in fairly close agreement (Table I). The equations of rotatory dispersion for these eleven salts are reproduced in Tables II-XII for the sake of comparison.

**The Effect of Constitution on the “Characteristic” Absorption Band in the Ultra-Violet Region**

The wavelength of the “Characteristic” absorption band of anilino-camphor-β-sulphonates is 3613 Å. U. The replacement of an hydrogen atom by a methyl group in the corresponding toluidino salts has shifted this band further to the ultraviolet end of the spectrum and the order of this shift in different position isomerides is as follows (Table I, Nos. 1, 2, 3, 4):

\[ m > o > p > un. \]

If the substituent group is iodine, the shift of the “Characteristic” absorption band is towards the red end of the spectrum and the order is as follows (Table I, Nos. 1, 5, 6, 7):

\[ m > o > p > un. \]
The substitution of the pyridine ring for the benzene nucleus (Table I, Nos. 1 and 8) produces a shift of about 323 Å. U. in the wavelength of the "Characteristic" absorption band towards the ultraviolet side, whereas the thiazole ring (Table I, Nos. 1 and 9) produces a similar but much smaller shift (about 73 Å. U.). The substitution of the sulphonamido group in the para position for an hydrogen atom in the benzene nucleus (Table I, Nos. 1 and 10) produces, however, a small shift of about 59 Å. U. to the red end of the spectrum. The substitution of 6-methoxyquinoline ring for the phenyl group produces a remarkably large shift of about 462 Å. U. of the "Characteristic" absorption band towards the ultraviolet end of the spectrum (Table I, Nos. 1 and 11).

The effects of dispersion can be eliminated from both the Drude as well as the Maxwell-Sellmeier equations by making $\lambda^2 - \lambda_0^2 = 1$; in the case of the Drude equation the value of rotatory power becomes equal in magnitude to that of $k_0$, the rotation constant. The value of refractive index, $n_{abs}$, in the Maxwell-Sellmeier equation for the corresponding wavelength $\lambda$, where $\lambda^2 = 1 + \lambda_0^2$, may be taken as the absolute measure of the refractive index of the medium in which the effect of wavelength, i.e., dispersion, is eliminated as in the case of the values of $k_0$.

A comparison of $k_0$ with $n_{abs}$ or $\sqrt{a^2 + b_0 (1 + \lambda_0^2)}$, however, reveals no simple relationship: in the case of toluidino camphor-β-sulphonates when $k_0$ decreases, the corresponding values of $n_{abs}$ also decrease. On the other hand in the case of iodanilino salts the result is opposite.

THE NATURE OF THE RACEMIC FORMS OF THE CAMPHOR-β-SULPHONATES

A glance at Tables II-XII reveals that the refractive indices of the dextro and the racemic forms in the visible spectrum for 5 wavelengths ($\lambda_{4708}$ to $\lambda_{4558}$) are identical in 1% (or less) aqueous solution within the limits of experimental error. In the absence of any differences in the values of refractive indices of the two forms in dilute solutions, it is not possible to draw any unequivocal conclusion regarding the nature of the racemic modification.

THE ROTATORY AND REFRACTIVE DISPERSION STUDIES AS AN AID IN THE DETERMINATION OF THE CHARACTERISTIC ULTRAVIOLET ABSORPTION BANDS; ANALOGY WITH RAMAN SPECTRA IN THE INFRA-RED REGION

We have seen that our studies of refractive and rotatory dispersion, using the Maxwell-Sellmeier and the Drude equations respectively, give us
The Refractive Dispersive Power of Organic Compounds—II

almost identical values of \( \lambda_0 \)—the wavelengths of the dominant absorption bands of the molecules in the ultraviolet region of the spectrum (Table I). We have not verified these bands by direct measurements in the present work but in Part I of this series\(^1\), the values of the dominant absorption bands for camphor in the ultraviolet region obtained from dispersion data were found to agree with those determined by direct absorption measurements. The utility of rotatory and refractive dispersion studies is thus evident: it has brought the study of the ultraviolet absorption spectra within the region of the visible spectrum technique. The case is, therefore, analogous to the Raman spectra which has enabled the determination of the position of the infra-red absorption bands of molecules by measurements in the visible region.

**Experimental**

The compounds described in this paper were prepared and purified by methods described elsewhere.\(^5\)

The refractive indices were determined with a Pulfrich Refractometer: water maintained at 33–35° C. was circulated through the jacketed mount of the observation cell containing the solution. The concentration of the aqueous solutions of the salts was 1% (namely, 1·0 gram in 100 c.c. of the solution) except in the case of \( o-, m- \) and \( p- \) iodonilinocamphor-\( \beta \)-sulphonates for which 0·5% solution were used. The experimental results are given in Tables II–XII.

**Summary**

1. The refractive dispersion of salts of camphor-\( \beta \)-sulphonic acid \( (d- \) and \( dl- \)) with eleven primary aromatic and heterocyclic bases was determined in aqueous solution for five wavelengths \( (\lambda_{6708} \text{ to } \lambda_{4358}) \). The results can be accurately represented by the Maxwell-Sellmeier equation, using only one term of the summation.

2. It is found that the values of the wavelengths of the "Characteristic" absorption bands \( (\lambda_0) \) deduced from the present measurements on refractive dispersion of these salts are almost identical with those deduced from the rotatory dispersion measurements previously described.

3. The effect of replacement of an hydrogen atom of the phenyl group in anilinocamphor-\( \beta \)-sulphonate by different groups has been discussed.

4. The values of the refractive dispersion of the dextro and the racemic salts are identical in dilute solution.

5. The utility of the dispersion studies for the determination of the dominant absorption bands of the molecules in the ultraviolet region has
been stressed and its analogy with Raman spectra for infra-red absorption bands pointed out.

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2. Gladstone and Dale
3. Lorentz
4. Maxwell
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