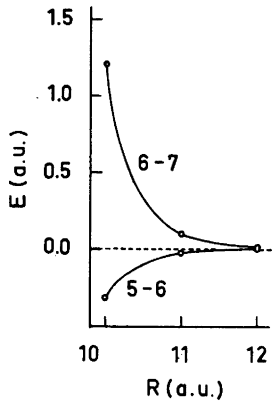

Fig. 2. Dipole-dipole interaction energies over distance R.

development of the charge distribution starts with a term containing the dipole moment of the charge distribution. The bond dipole moments may be obtained from quantum mechanical calculations if they are not measurable.[4]

As an example the hindered inner rotation of ethane may be considered. Setting the bond moments $\vec{p}_i$ at the center of the C—H bond one can compute their interaction energies by

$$E_{12}=(\vec{p}_1\vec{p}_2-3\vec{r}_{12}\vec{p}_1\cdot\vec{r}_{12}\vec{p}_2/r_{12}^2)/|r_{12}|^3$$

with $\vec{r}_{12}$ being the vector from the first to the second dipole moment. For the energy barrier of 1.2 kcal/mole about 50 % of the measured value is obtained. The position of the two hydroxyl groups of catechol was measured. For this example, calculation yields correct values for the bond energy of the hydrogen bridge.

In the α-tocopheryl radical the most favoured position of the methyl groups was selected by estimating the minimum dipole-dipole interactions out of one thousand positions of rotation. Next, the energy diagrams for two α-tocopheryl radicals were calculated; in the first model positions 5 and 6 are approaching one another, in the second case positions 6 and 7 (Fig. 1). Fig. 2 shows the corresponding energy diagrams. The interaction energies may not quantitatively be correct for smaller distances. The most important result, however, is the different shape of the two diagrams. An approach of positions 6 and 7 results in a repulsion curve, while in an approach of positions 5 and 6 the energy decreases, thus allowing for disproportionation.

These results support the following experimental evidence: monovalent oxidation of α-tocopherol proceeds *via* the α-tocopheryl radical (phenoxy radical) to the intermediary *ortho*-quinone methide,[5,6] finally yielding a single spirodienone ether.[5] The favoured reactivity of position 5 which results in the formation of ether bonds at this position in all examples has been observed by Nilsson *et al.*[6] for the tocols and chromanols. Computation of the dipole-dipole interactions of these model compounds in a fashion analogous to α-tocopherol confirms these results.

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Note on the Pigments of Some *Drosera* Species

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7-Methyljuglone (5-hydroxy-7-methyl-1,4-naphthoquinone) and plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone) seem to be fairly common constituents of many *Drosera* species although their co-occurrence has previously only been proved in two of seventeen investigated species.[1] We now report their co-occurrence in three more species. As earlier reported[2] both *Drosera intermedia* and *D. anglica* contain plumbagin, 3-chloroplumbagin, 2-methylnaphthazarin (5,8-dihydroxy-2-methyl-1,4-

naphthoquinone) and a fourth quinone tentatively identified as 7-methyljuglone. The identity of this quinone has now been established by comparing its spectral and chromatographic properties with an authentic specimen.

7-Methyljuglone and plumbagin have also been isolated from *D. rotundifolia*, from which plumbagin has been obtained earlier,[3] although 7-methyljuglone seems to be the main quinone. No traces of 3-chloroplumbagin or 2-methylnaphthazarin could be found in *D. rotundifolia*, but it contains a very small amount of a blue steam volatile pigment. The mass and electronic spectra of the crude product suggest that it is not related to the above mentioned naphthoquinones. It will be further investigated.

The anthocyanins of *D. rotundifolia* are the same as those found in the two other species *viz.* cyanidin and pelargonidin glycosides proved by spectral and chromatographic data.

Plumbagin has hitherto been synthesised by two alternative methods both involving a large number of stages.[4,5] A somewhat shorter route is to prepare plumbagin by dechlorination of 3-chloroplumbagin, easily obtained from juglone, with Raney nickel alloy in alkaline solution followed by oxidation with ferric chloride. The same method has also been used for preparing 7-methyljuglone from 8-chloro-7-methyljuglone.

Experimental. The absorption spectra were recorded on a Spectronic 505 spectrophotometer. The molecular weights and the mass spectra were determined with an LKB 9000 mass spectrometer. Preparative TLC and co-chromatography were performed as earlier reported.[2] The same solvent systems were also used. All melting points are uncorrected.

D. rotundifolia was collected at Dorotea in southern Lappland. The origin of the other two *Drosera* species, the extraction procedure and the first separation step have been described earlier.[2]

D. intermedia and *D. anglica*. The third band obtained by preparative TLC in benzene-chloroform (2:3, v/v) yielded after elution a yellow pigment. It was identified as 7-methyljuglone by comparison with a synthetic sample, m. p. 125.5–126.5°C (mass spectra, UV, IR).

D. rotundifolia. Preparative TLC in benzene-chloroform (2:3, v/v) gave:

Band 1 (R_F: 0.70) yielded after elution a trace of a yellow pigment identified as plumbagin (UV, co-chromatography).

Band 2 (R_F: 0.50) contained a yellow pigment m.p. 97–101°C. Spectral and chromatographic data established its identity with 7-methyljuglone.

Band 3 (R_F: 0.01–0.02) gave after elution a very small amount of a blue pigment. λ_{max} (EtOH, 99.5 %) 264, 635 nm. MS: *m/e* 237 (65 %); 236 (15 %); 235 (100 %); 165 (31 %); 73 (28 %); 61 (35 %); 43 (47 %).

The methods used for separation, hydrolysis and identification of the anthocyanidins were the same as those reported earlier.[2]

Synthesis of plumbagin. To the stirred solution of 3-chloroplumbagin [6] (0.2 g) in sodium hydroxide (2 N, 150 ml) was added Raney nickel alloy (5 g) in small portions. After attaining room temperature the solution was filtered and acidified (2 N hydrochloric acid). After addition of a solution of crystallised ferric chloride (5 g) in hydrochloric acid (0.5 N, 26 ml) to the filtrate it was stirred for one hour and then steam distilled. Filtration and ether extraction gave 0.07 g of a crude product (40 %) m.p. 69–72°C. Mass spectrometric and chromatographic analyses proved that it contained, besides plumbagin, 2-methyl naphthazarin and traces of unchanged material. After recrystallisation from aqueous ethanol the melting point was raised to 72–75°C. Spectral data established its identity with an authentic specimen.

7-Methyljuglone was prepared from 8-chloro-7-methyljuglone [7] by the above mentioned dechlorination method. After recrystallisation from light petroleum the crude product (30 %) melted at 125–126°C. Spectral data established its identity with a specimen prepared according to Cooke and Dowd.[8]

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