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CHEMICAL INVESTIGATION OF THE STEM-BARK OF *CEDRUS DEODARA*

ISOLATION OF A NEW DIHYDROFLAVONOL, *DEODARIN*

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Abstract—A new dihydroflavonol named deodarin has been isolated from the stem-bark of *Cedrus deodara*. From a detailed study of its reactions and spectra, it has been tentatively assigned the constitution 3′,4′,5,6-tetrahydroxy-8-methyl dihydroflavonol.

THE family *Pinaceae* of the order coniferales, has yielded a variety of natural products comprising alkaloids, phenol glycosides, flavonoid compounds, lignans, tannins, resins, mono and sesquiterpenes and diterpene acids. It is divided into three subfamilies, *Abietoidae*, *Laricoidae* and *Pinoidae*. The *Cedrus* genus belonging to the subfamily *Laricoidae* has not been subjected to a systematic study of their polyphenols, the only work so far carried out being a qualitative chromatographic study of the distribution of taxifolin-3′-glucoside in *Cedrus atlantica* (probably, var. glauca).[1] We have now examined the stem-bark of *C. deodara* in detail. The waxy material in the bark was removed with petroleum ether and the subsequent benzene extraction yielded a terpenoid. Further extraction with ether afforded a new dihydroflavonol, deodarin, in 0·15% yield.

Deodarin has a molecular formula $C_{16}H_{14}O_7$, melts with decomposition at 248–251°, is dextro rotatory and gives the characteristic colour reactions of a dihydroflavonol (Shinoda's, Pew's and Pacheco's tests). The UV spectrum agrees with the characteristics of a dihydroflavonoid system. The presence of an absorption band at 1653 cm^{-1} in the IR spectrum indicates the presence of a chelated carbonyl. Methylation of deodarin employing excess of dimethyl sulphate gives a tetramethyl ether with a UV spectrum similar to that of the parent dihydroflavonol. The absence of ferric reaction and the presence of a band at 1672 cm^{-1} (non-chelated carbonyl) in the IR spectrum clearly indicate that all the phenolic hydroxyls have undergone methylation. A strong absorption band at 3546 cm^{-1} still present shows that the alcoholic hydroxyl group originally present has not undergone methylation.

Iodine oxidation[2] of deodarin yields a flavonol, of molecular formula $C_{16}H_{12}O_7$. It has no methoxyl group but possesses one C-methyl group and forms a pentamethyl ether and a penta-acetate. The alkali degradation of the pentamethyl ether yields veratric acid, thereby proving the presence of 3′,4′-oxygenation pattern. This is also supported by the bathochromic shift (19 mμ) in the higher wavelength band of the flavonol in the UV spectrum, on the addition of boric acid and sodium acetate.[3] The absence of any bathochromic shift in the lower wavelength band of the flavonol after

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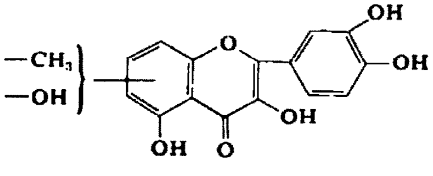
[2] V. B. Mahesh and T. R. Seshadri, *Proc. Indian Acad. Sci.* 41A, 210 (1955).

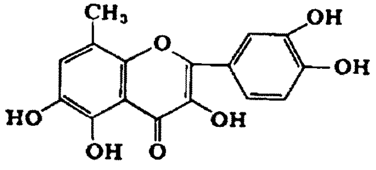
[3] L. Jurd, *Arch. Biochem. Biophys.* 63, 376 (1956).

addition of sodium acetate, denotes the absence of a free hydroxyl group in the 7-position.[4] In order to prove whether a hydroxyl group is present in the 5-position of the flavonol, its partial methyl ether was prepared (using four moles of dimethyl sulphate). It gives a green colour with brownish tinge with alcoholic ferric chloride and also shows a bathochromic shift (10 mμ) by addition of aluminium chloride. Thus the flavonol possesses hydroxyls in the 3',4'- and 5-positions leading to the partial formula I. This leaves the assignment of the fifth hydroxyl group and the C-methyl group in the condensed benzene ring.

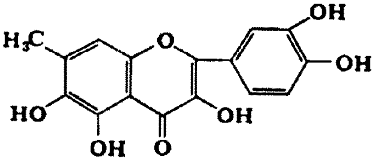


I

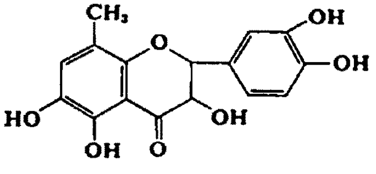
The "gossypetone reaction"[5] for the presence of a *para*-substituted dihydroxyl system was negative and this conclusively rules out the location of the fifth hydroxyl in the 8-position. Addition of boric acid has not only caused a bathochromic shift of the higher wavelength band (*vide supra*) but has also resulted in the lower wavelength band suffering a bathochromic shift (8 mμ). It has been shown in the case of herbacetin[6] and other flavanols, that the presence of *o*-dihydroxyl group in the condensed benzene ring, results in the lower wavelength band experiencing such a bathochromic shift. This would suggest that the fifth hydroxyl is located in the 6-position, giving rise to a *o*-dihydroxylic system in the condensed benzene ring which also explains the positive Bargellini test. There are only two positions available for the C-methyl group, leading to the alternative structures II and III for the flavonol. So far, among the naturally occurring flavonoids, there is no case of a C-methyl group being present in the 7-position and biogenetic considerations also exclude this and hence the probable structure II for the flavonol leads to the structure IV for deodarin.



II



III



IV

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The NMR spectrum of deodarin methyl ether lends support to the presence of four methoxyls and one C-methyl group on a dihydroflavonol skeleton. However the signals due to aromatic protons were difficult to interpret as part of the aromatic spectrum merged with the $CHCl_3$ signal.

EXPERIMENTAL

The UV spectra were taken on a Perkin-Elmer Model 4000-A, Spectracord. The IR spectra were recorded on a Perkin-Elmer Infracord Model 137 spectrophotometer. The NMR spectrum was determined in $CDCl_3$ containing tetramethylsilane as internal reference on a Varian H.R. 60 spectrometer.

Isolation of deodarin (IV). The fresh air-dried stem-bark (5 kg) was extracted successively with pet. ether, benzene and ether. While the pet. ether extract yielded mainly waxy material, the benzene extract gave a residue which had terpenoid properties. From the ether extract was obtained a yellow crystalline solid (7·5 g) which on crystallization from acetone–benzene yielded pale yellow needles of deodarin, m.p. 248–251° with dec. (Found: C, 59·2; H, 5·2; $C_{16}H_{14}O_7$, ½ H_2O requires: C, 58·8; H, 4·8%) $[\alpha]_D^{26°}$ +28·5° (*c*, 1·05 in acetone.) UV $\lambda_{\max}^{\mathrm{EtOH}}$ in mμ 290(log ε 4·09) and 330(infl); $\lambda_{\max}^{\mathrm{EtOH+NaOAc}}$ in mμ 290(infl) and 330(4·14); $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ in mμ 300(3·84); IR $\nu_{\max}$ (KBr) 3509, 1653, 1600, 1282, 1120 and 1089 cm^{-1}. It gave an intense purple colour with alcoholic $FeCl_3$ and a deep red colour with both Mg and HCl and Zn and HCl. It did not respond to the gossypetone test.

Methylation of deodarin (IV). A solution of deodarin (0·50 g) in dry acetone (200 ml) was refluxed with dimethyl sulphate (2 ml) and anhydrous K_2CO_3 (6 g) for 15 hr. The product crystallized from benzene–MeOH as colourless needles, m.p. 215–216°. It did not give any colour with alcoholic $FeCl_3$. (Found: C, 63·9; H, 6·4; —OCH_3, 32·5; $C_{20}H_{22}O_7$ requires: C, 64·2; H, 5·9; four —OCH_3 33·1%.) UV $\lambda_{\max}^{\mathrm{EtOH}}$ in mμ 279 and 315 (qualitative); IR $\nu_{\max}$ (KBr) 3546, 1672 cm^{-1}; NMR spectrum: signals at 4·81 τ (doublet, J = 11 c/s) C-2 proton, 5·34 τ (doublet, J = 11 c/s). C-3 proton, 5·83, 5·86, 5·93 τ (singlets) —OCH_3 (12 protons) and 7·60 τ (singlet) C—CH_3 (3 protons).

Acetylation of deodarin (IV). A mixture of deodarin (0·10 g), acetic anhydride (1 ml) and dry pyridine (2 ml) was kept at room temp for 24 hr. It was poured into crushed ice and the product crystallized from ethyl acetate—pet. ether as colourless needles, m.p. 145–147°. (Found: C, 58·9; H, 5·0; $C_{26}H_{24}O_{12}$ requires: C, 59·1; H, 4·6%.)

Dehydrogenation of deodarin to flavonol (II). A mixture of deodarin (0·50 g) and fused potassium acetate (3·0 g) in glacial acetic acid (30 ml) was heated under reflux and I_2 (0·50 g) in glacial acetic acid (20 ml) was added in small lots during 1 hr. After refluxing for a further 3 hr, acetic acid was removed under red. press. and SO_2-water added to the residue. The product crystallized from acetone–pet. ether as yellow needles (0·30 g), m.p. 290–292°. With alcoholic $FeCl_3$ it gave a green colour with brownish tinge. With conc. H_2SO_4 it exhibited a green fluorescence. (Found: C, 57·5; H, 4·7; C—CH_3, 2·3; $C_{16}H_{12}O_7$,H_2O requires: C, 57·5; H, 4·2; One C—CH_3, 4·7%; sample dried at 180° for 8 hr. Found: C, 59·7; H, 4·5; $C_{16}H_{12}O_7$ requires: C, 60·8; H, 3·8% showing that still some water of crystallization is held tenaciously.) UV $\lambda_{\max}^{\mathrm{EtOH}}$ in mμ 255 (log ε 4·18), 295 (infl) and 375 (4·19); $\lambda_{\max}^{\mathrm{EtOH+NaOAc}}$ in mμ 257·5, 298 (infl) and 381; $\lambda_{\max}^{\mathrm{EtOH+H_3BO_3+NaOAc}}$ in mμ 263, 300 (infl) and 394; $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ in mμ 267 and 430; IR $\nu_{\max}$ (KBr) 3509, 1664, 1618, 1359, 1202, 1092 cm^{-1}.

Methylation of the flavonol (II). A mixture of the flavonol (0·20 g) in dry acetone (100 ml), freshly ignited K_2CO_3 (4·0 g) and dimethyl sulphate (1 ml) was refluxed for 40 hr. The product crystallized from ethyl acetate–pet. ether as colourless needles, m.p. 150–151°. It gave no colour with alcoholic $FeCl_3$. (Found: C, 64·7; H, 5·7; —OCH_3, 39·3; $C_{21}H_{22}O_7$ requires: C, 65·3; H, 5·7; five —OCH_3, 40·2%.) UV $\lambda_{\max}^{\mathrm{EtOH}}$ in mμ 241, 267 and 342; IR $\nu_{\max}$ (KBr) 1637, 1616, 1274, 1235, 1111, 1057 and 1042 cm^{-1}.

Acetylation of the flavonol (II). A mixture of the flavonol (0·10 g) in dry pyridine (2 ml) and acetic anhydride (1 ml) was kept at room temp for 24 hr. It was poured into crushed ice and the product crystallized from alcohol as needles, m.p. 178–180°. (Found: C, 58·9; H, 4·2; $C_{16}H_{22}O_{12}$ requires: C, 59·3; H, 4·2%.)

Partial methylation of the flavonol (II). The flavonol (0·10 g) when heated under reflux for 6 hr in acetone (50 ml) with dimethyl sulphate (0·15 ml; 4 moles) and anhydrous K_2CO_3 (1·0 g) gave its tetramethyl ether which crystallized from MeOH as pale yellow hexagonal crystals, m.p. 166–168°. With alcoholic $FeCl_3$ it gave a green colour with brownish tinge. (Found: C, 64·0; H, 5·6; $C_{20}H_{20}O_7$ requires: C, 64·5; H, 5·4%.) UV $\lambda_{\max}^{\mathrm{EtOH}}$ in mμ 254 and 345; $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ in mμ 254 and 355.

Alkali fission of the flavonol methyl ether. The flavonol methyl ether (40 mg) in alcoholic potash (50%; 10 ml) was refluxed for 2 hr. The solution was acidified and the alcohol removed under red. press. The solid that separated was taken up in ether and from the ether extract the acid component was extracted into $NaHCO_3$ aq. The bicarbonate extract was acidified and shaken with ether. Evaporation of the ether left a residue which crystallized from hot water as colourless needles m.p. 178°, alone or admixed with an authentic sample of veratric acid, R_f value 0·41 in butanol saturated with aqueous ammonia (using bromophenol blue as the developing agent).

The residual ether layer on evaporation yielded a small amount of sticky solid which gave a D.N.P. derivative, obtained as red needles from ethyl alcohol, m.p. 170–171°.