Flavonoids and Related Compounds in Leaves of Pinaceae, IV*

Flavonoids of *Cedrus deodara* (Roxb.) G. Don ex Loud.

H. H. van Genderen and J. van Schaik

Botanical Laboratory, State University of Utrecht, Lange Nieuwstraat 106, 3512 PN Utrecht, The Netherlands

Z. Naturforsch. **35 c,** 342–343 (1980);
received December 28, 1979

Cedrus deodara, Pinaceae, Flavonoids

Several flavonoids were isolated from needles of *Cedrus deodara.* Among them were the 3-glucosides of kaempferol, isorhamnetin and syringetin. Apigenin-7-glucoside and presumably an alkylkaempferol-3-diglucoside were also present. Kaempferol-3-glucoside occurred both free and acylated with *p*-coumaric acid and/or ferulic acid.

Introduction

Needles of some Pinaceae species have been analysed in our laboratory especially for phenolic acids and flavonoids [1] and recently also for triterpenoids [2]. In this paper the flavonoid analysis of *Cedrus deodara* needles is described.

Previously Takahashi *et al.* [3] have demonstrated the presence of two unspecified flavonoid glycosides in deodar needles. Adinarayana and Seshadri [4] have isolated a C-methyldihydroflavonol from the stem bark of the same cedar species. Deodarin, as they have called it, was supposed to be 3,5,6,3′,4′-pentahydroxy-8-methyldihydroflavone. The flavonoids in the needles of cedar species, apart from *C. atlantica* [5], have not yet been studied in detail [6].

Materials and Methods

Branchlets of *Cedrus deodara* (Roxb.) G. Don ex Loud. (Pinaceae) were collected at the Blijdestein Pinetum in Hilversum, The Netherlands, in August 1976. A voucher specimen was deposited at the Herbarium of Utrecht University.

Fresh needles were freeze-dried. The acetone extract from 95 g dry needles was concentrated and distributed over water-light petrol, the acidic water layer was subsequently extracted with butanol. The flavonoids in the butanol extract were separated by cellulose column chromatography. The identity of the compounds was established by standard methods [7–9]. In addition purity was checked by reversed-phase high-performance liquid chromatography [2, 5]. Degradation – or hydrolysis products were analysed by paper-, thinlayer – and/or gas-liquid chromatography.

Results and Discussion

A variety of flavonoids appeared to be accumulated in deodar needles. Only a few of them had been purified in sufficient amounts to elucidate their structures.

One flavone glycoside and three flavonol glycosides could be identified as apigenin-7-glucoside and kaempferol-, isorhamnetin-, and syringetin-3-glucoside respectively.

Two other types of flavonol glycosides were partly identified. One of them, compound No **8** (Tables I and II), appeared to be a diglycoside of a kaempferol-like compound; its aglycone (**3**) had spectral properties closely related to kaempferol (Table I). By paper- and polyamide-thinlayer-chromatography, however, **3** could be separated from kaempferol (**1**) and some of its derivatives (Table II). The main phenolic acid formed as acid degradation product of **8** was *p*-hydroxybenzoic acid, as can be expected from flavonoids with a 4′-hydroxylated B-ring [13]. Only traces of phloroglucinol were found after $Ba(OH)_2$ degradation of **3**, but the main product behaved as an alkyl substituted phloroglucinol on gaschromatographic analysis of the trimethylsilyl derivatives. The degradation products and the chromatographic- and spectral properties of **3** indicate that it is a 6- or 8-alkylkaempferol, probably 6-methylkaempferol. The glycoside **8** of flavonol **3** was a 3-glycoside according to spectral shifts. H_2O_2 degradation [14] demonstrated the presence of a diglycoside and acid hydrolysis liberated glucose and some rhamnose; so compound **8** was likely to be 6-methylkaempferol-3-rutinoside. In other diglycoside fractions of the same aglycon **3** only glucose or both glucose and fructose were found as composing monosaccharides. In these cases the 3-diglucoside and the 3-fructoglucoside or glucofructoside of **3** can be expected as well. Possibly due to its instability,

---

* Part III: G. J. Niemann, Z. Naturforsch. **33 c,** 777 (1978).

Reprint requests to H. H. van Genderen.

0341-0382/80/0300-0342 $ 01.00/0

Table I. UV absorption maxima and shoulders (sh) of some flavonoids and their spectral shifts of band II (short wavelengths) and of band I (long wavelengths) with diagnostic reagents [9] in nm. **1:** kaempferol; **2:** 6-methylkaempferol [10]; **3:** aglycon of **8; 4:** 3,5,6,4′-tetrahydroxy-8-methylflavone [11]; **5:** 4′-methylkaempferol; **6:** kaempferol-3-glucoside; **7:** 6-methylkaempferol-3-glucoside [10]; **8:** glycoside of **3; 9:** 5,6,4′-trihydroxy-3-methoxy-8-methylflavone [11]; **10:** aglycon of **11; 11:** acylated glycoside of **10.** Spectra were measured in 70% ethanol. Literature data were from measurements in methanol.

Substance	UV spectrum	Bathochromic shifts with diagnostic reagents						
		Na OAc		NAOEt	$AlCl_3$	$AlCl_3 + HCl$	$NaOAc + H_3BO_3$	
		(II)	(I)	(I)	(II)	(II)	(II)	(I)
1	257, 295, 322, 366	15	12	59	1	− 2	3	2
2	254 sh, 270, 300, 333 sh, 366	5	24	51	2	?	?	?
3	263, 298, 364	14	21	53	8	9	2	1
4	271, 300, 368	1	7	52	2	1	0	0
5	265, 295 sh, 320, 365	10	19	50	3	3	2	1
6	265, 300 sh, 353	9	22	34	7	7	0	0
7	270, 335	5	51	65	8	10	?	?
8	265, 305, 345	10	21	35	9	9	3	0
9	271, 300, 338	0	30	60	0	3	0	1
10	265, 293, 315, 364	8	14	45	5	5	2	1
11	268, 300 sh, 312, 345	7	20	15	10	10	0	0

Table II. HRf values of some flavonoids in different chromatographic systems. P-A = polyamide thinlayer in chlorophorm : methanol : methylethylketone = 9 : 4 : 2 [12]. The other chromatograms were paperchromatograms on Whatman no 1 paper; BuAW = butanol: 27% acetic acid = 1 : 1; H_2O = demineralized water; HOAc = 15% acetic acid; Phe = phenol saturated water.

Substance	P-A	BuAW	H_2O	HOAc	Phe
Kaempferol (**1**)	42	85	–	–	–
3 (aglycon of **8**)	58	84	–	–	–
4′-Methylkaempferol (**5**)	72	–	–	–	–
Rhamnetin	55	69	–	–	–
Isorhamnetin	52	–	–	–	–
Kaempferol-3-glucoside (**6**)	–	70	12	44	72
8 (glycoside of **3**)	–	71	13	50	82
11 (acylated flavonoid)	–	90	3	7	95

fructose untill now is seldom found in flavonoids in general [5] and not yet demonstrated before in Pinaceae flavonoids [1].

The second type of partly identified glycosides was an acylated flavonol glucoside (**11**). Kaempferol-3-glucoside, *p*-coumaric acid and some ferulic acid were the products of alkaline hydrolysis. This indicates the presence of kaempferol-3-*p*-coumaroylglucoside and kaempferol-3-feruoylglucoside though a double acylation cannot be excluded.

The systematic relation of *Cedrus* with *Larix*, *Abies* and other Pinaceae, which might have been reflected in the chemical composition of the needles, will be discussed elsewhere [15].

Acknowledgements

The authors wish to thank Mr. G. Bootsman for placing the deodar samples at their disposal and Dr. G. J. Niemann for his aid in the flavonoid identification.

[1] G. J. Niemann, Acta Bot. Neerl. **28,** 73 (1979).

[2] G. J. Niemann and W. J. Baas, Acta Bot. Neerl. **27,** 229 (1978).

[3] M. Takahashi, T. Ito, A. Mizutani, and K. Isoi, J. Pharm. Soc. Japan **80,** 1488 (1960).

[4] D. Adinarayana and T. R. Seshadri, Tetrahedron **21,** 3727 (1965).

[5] G. J. Niemann, Z. Naturforsch. **32 c,** 1015 (1977).

[6] J. B. Harborne, T. J. Mabry, and H. Mabry, The Flavonoids, Chapman and Hall, London 1975.

[7] J. B. Harborne, Comparative Biochemistry of the Flavonoids, Academic Press, London and New York 1967.

[8] P. Ribéreau-Gayon, Les Composés Phénoliques des Végétaux, Dunod, Paris 1968.

[9] T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer-Verlag, Berlin-Heidelberg-New York 1970.

[10] R. Higuchi and D. M. X. Donnelly, Phytochemistry **17,** 787 (1978).

[11] S. A. Medvedeva, S. Z. Ivanova, N. A. Tyukavkina, and G. G. Zapesochnaya, Khim. Prir. Soedin. **13,** 650 (1977) (English Translation: Chem. Nat. Comp. **13,** 539 (1978)).

[12] K. Egger and M. Keil, Z. Anal. Chemie **210,** 201 (1965).

[13] G. J. Niemann, J. Chromatogr. **74,** 155 (1972).

[14] B. V. Chandler and K. A. Harper, Aust. J. Chem. **14,** 586 (1961).

[15] G. J. Niemann and H. H. van Genderen, Biochem. Syst. Ecol. (accepted for publication).