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TWO LIGNANS FROM *CEDRUS DEODARA**

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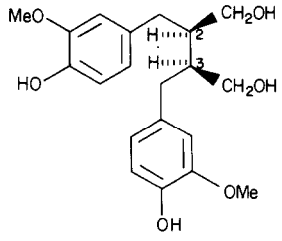
Key Word Index—*Cedrus deodara*; Pinaceae; wood: *meso-seco*isolariciresinol; cedrusinin; 1, 4-diarylbutane lignan; benzofuranoid neolignan.

Abstract—Two new lignans were isolated from the lead acetate-purified butanol–soluble fraction obtained from the wood of *Cedrus deodara*. They were identified as *meso-seco*isolariciresinol and cedrusinin respectively.

In an earlier communication[1] the isolation of lignoid polyphenolics from the lead acetate-purified butanol-soluble fraction of the extractive of *Cedrus deodara* wood was described. The initial eluates of cellulose column chromatography of this fraction yielded lariciresinol and dihydrodehydroconiferyl alcohol (substances F and G, respectively) on further Si gel chromatography. The other eluates of this Si gel column, on further processing, led to the isolation of two other components, named F1 and G1, which are described here.

Substance F1 (*meso-seco*isolariciresinol), $C_{20}H_{26}O_6$, M^+ *m/z* 362, showed IR bands for hydroxyl groups and aromatic rings. Its ^1H NMR spectrum exhibited signals attributable to two aliphatic methines, a pair of benzylic methylenes at δ 2.55, two hydroxymethylenes at δ 3.50, two aryloxymethyls at δ 3.73 and six aromatic protons characteristic of an ABC trisubstituted aromatic system. The presence of two primary and two phenolic hydroxyl groups was confirmed by the formation of a tetra-acetyl derivative whose IR and ^1H NMR spectra displayed an aliphatic acetoxymethyl signal (δ 2.05) with carbinolic methylene doublets at δ 4.12, 4.20 and a phenolic acetoxy methyl signal at δ 2.28. Consistent with the 1, 4-diarylbutane structure, its mass spectrum exhibited an ion at *m/z* 181 caused by symmetrical scission of the molecule. The most prominent peak at *m/z* 137 provided further evidence for the presence of a methoxyl and a hydroxyl in each benzyl unit.

*CDRI communication No. 2995.



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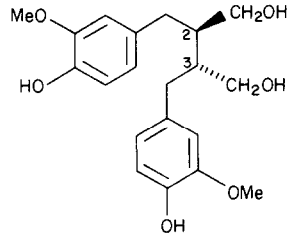

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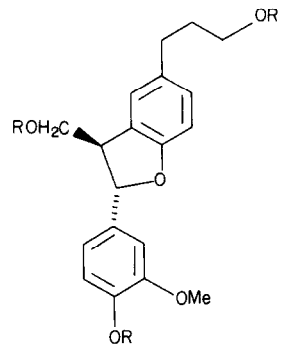

3 R=H
3a R=Ac

Table 1. ^{1}H NMR chemical shifts (multiplicities in parentheses) of H_2-7, 7′, H-8, 8′ and H_2-9, 9′ in substance F1, *seco*isolariciresinol and *meso-seco*isolaricirisinol

Compound (solvent)	H_2-7, 7′	H-8, 8′	H_2-9, 9′	Ref.
Substance F1 ($CDCl_3$)	2.55 (*d*)	1.83 (*m*)	3.50 (*m*)	—
Substance F1 tetra-acetate ($CDCl_3$)	2.70 (*d*) $J = 7$ Hz	2.18 (*m*)	4.12, 4.20 (each *d*) $J = 5$ Hz	—
*Seco*isolaricire sinol (CD_3OD)	2.60, 2.62 (each *d*) $J = 6.8$ Hz	1.92 (*m*)	3.59 (*d*)	[3–5]
*Meso-seco*isolari-ciresinol (CD_3OD)	2.60 (*d*) $J = 7.5$ Hz	2.00 (*m*)	3.62 (*m*)	[3–5]
*Seco*isolaricire-sinol tetra-acetate ($CDCl_3$)	2.67 (*d*) $J = 7.5$ Hz	2.17 (*m*)	4.02, 4.25 (each *dd*) $J = 11.5$ Hz	[3, 4]

In view of the above considerations, the identification of the substance as *meso-seco*isolariciresinol (8*R*, 8′*R*) (**1**) was considered plausible because it was optically inactive. *Seco*isolaricirosinol (8*R*, 8′*S*) (**2**), on the other hand, is reported to show $[\alpha]_D = -30.8°$ [2]. This was confirmed by a comparative study of the ^{1}H NMR spectra of substances F1, *seco*isolaricirosinol, synthetic *meso-seco*isolaricirosinol and tetra-acetates of substance F1 and *seco*isolaricirosinol and the chemical shifts and couplings of the related 7, 8, 9-protons in these substances (Table 1).

*Meso-seco*isolariciresinol has been reported as a synthetic product [5] obtained by hydrogenolysis of a lignan from Norway spruce. This is the first report of its occurrence as a natural product.

Substance G1 (cedrusinin), $C_{19}H_{22}O_5$, M^+ *m/z* 330, UV maxima at 281 nm, indicated the presence of the 2-aryl-3,5-dialkylbenzofuran chromophore in the molecule [6–8]. The IR spectrum exhibited bands for hydroxyl groups (3400, 1030) and aromatic rings (1600, 1482 cm^{-1}). Its ^{1}H NMR spectrum showed signals for a phenoxy methyl (δ 3.77), a methylol group, an oxymethine as a doublet (δ 5.40, $J = 7$ Hz), six aryl protons and a multiplet at δ 1.74, triplet ($J = 7$ Hz) at 2.58 and a triplet ($J = 5$ Hz) at 3.50 which were attributed to a *n*-propanol side-chain.

G1 yielded a triacetyl derivative **3a** whose IR bands (1760, 1728 cm^{-1}) and ^{1}H NMR signals, ascribable to two alcoholic (δ 2.03) and one phenolic acetoxy methyls (δ 2.29) and two carbinolic methylenes (δ 4.10, 4.40) suggested two primary and one phenolic OH groups. The mass spectral pattern of G1 exhibited prominent peaks at *m/z* 137 assignable to the *p*-hydroxy-*m*-methoxybenzylic ion, *m/z* 151 and other ions characteristic of dihydrobenzofuranoid neolignans. The structure of G1 was, therefore, assigned as **3**, 7-deoxycedrusin, as reported in an earlier communication [1].

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CDCl_3$ unless otherwise stated. Spots on Si gel TLC layers were detected with 5% anisaldehyde–H_2SO_4 in EtOH.

The lead acetate-purified BuOH fraction (20 g) was chromatographed on cellulose and the residue from the $CHCl_3$–MeOH–H_2O (35 : 1 : 2) eluate was again fractionated ($CHCl_3$ saturated with H_2O; $CHCl_3$–MeOH–H_2O, 35 : 3 : 2) on Si gel when fractions 11–14, showing a single spot on TLC, were concd to give a colourless, viscid liquid (F1), 0.18 g. The subsequent cellulose column eluate ($CHCl_3$–MeOH–H_2O, 35 : 3 : 2) was also chromatographed on Si gel ($CHCl_3$ saturated with H_2O; $CHCl_3$–MeOH–H_2O, 35 : 5 : 2) and the eluates 17–28 were concd to a residue which was again purified by prep. TLC on Si gel (C_6H_6–Me_2CO, 2 : 3) to afford G1 as a colourless, viscid syrup (0.13 g).

F1 (*meso-seco*isolariciresinol): UV (Me_2CO) nm: 332. IR (neat) cm^{-1}: 3400, 2925, 2850, 1595, 1505, 1455, 1425, 1360, 1262, 1208, 935, 825, 755. ^{1}H NMR (acetone-d_6): δ 1.83 (2H, *m*, H-8, 8′), 2.55 (4H, *d*, $J = 7$ Hz, H-7, 7′), 3.14 (4H, *m*, D_2O-exchangeable, OH-4, 4′, 9, 9′), 3.50 (4H, *m*, CH_2OH-9, 9′), 3.73 (6H, *s*, OMe-3,3′), 6.38–6.80 (6, Ar-H, ABC *m*). MS *m/z*, (rel. int): 362 (15) $[M]^+$, 344 (3), 189 (7), 181 (4), 163 (5), 151 (4), 150 (3), 138 (27), 137 (100), 131 (5), 122 (5), 94 (3). (Found: C, 65.34; H, 7.20; $C_{20}H_{26}O_6$ requires: C, 65.64; H, 7.13%).

Reaction of F1 (15 mg) with Ac_2O–pyridine gave a colourless syrup, R_f 0.62 ($CHCl_3$–MeOH, 99 : 1). IR (neat) cm^{-1}: 2920, 1760, 1738, 1728, 1604, 1510, 1365, 1278, 1230, 1200. ^{1}H NMR: δ 2.05 (6H, *s*, OCOMe-9, 9′), 2.28 (6H, *s*, OCOMe-4,4′), 2.70 (4H, *d*, $J = 7$ Hz, H_2-7, 7′), 3.77 (6H, *s*, OMe-3, 3′), 4.12, 4.20 (2H each, *d*, $J = 5$ Hz, CH_2OAc-9, 9′), 6.60 (2H, *dd*, $J = 1.5$, 8 Hz, H-5, 5′), 6.67 (2H, *d*, $J = 1.5$ Hz, H-2, 2′), 6.93 (2H, *dd*, $J = 1.5$, 8 Hz, H-6, 6′).

G1 (cedrusinin): $[\alpha]_D$ +4.21° (*c* 1.04, MeOH); UV (MeOH) nm: 217, 224, 279. IR (neat) cm^{-1}: 3400, 2820, 2750, 1600, 1482, 1372, 1270, 1235, 1200, 1155, 1118, 1030, 815, 752. ^{1}H NMR: δ 1.74 (2H, *m*, H_2-8′), 2.58 (2H, *t*, $J = 7$ Hz, H_2-7′), 3.50 (2H, *t*, $J = 5$ Hz, -CH_2OH-9′), 3.77 (3H, *s*, OMe-3), 3.50–4.0 (3H, *m*, H-8, -CH_2OH-9), 5.40 (1H, *d*, $J = 7$ Hz, H-7), 6.50–7.06 (6-ArH). MS *m/z* (rel. int.): 330 (54) $[M]^+$, 313 (16), 312 (72), 300 (41) $[M-CH_2O]^+$, 299 (19) $[M-CH_2OH]^+$, 298 (18) $[M-MeOH]^+$, 297 (16), 283 (12), 256 (30), 253 (19), 213 (14), 185 (15), 178 (12), 165 (18), 151 (30), 137 (40), 133 (38), 121 (35). (Found: C, 63.00; H, 6.70; $C_{19}H_{22}O_5$ requires: C, 63.03, H, 6.67%.)

G1 and Ac_2O–pyridine afforded a triacetyl derivative as an oil, $[\alpha]_D$ +109° (*c* 1.10, $CHCl_3$). IR (neat) cm^{-1}: 1765, 1738, 1602, 1485, 1365, 1226, 1194, 1115, 995. ^{1}H NMR: δ 2.03 (2H, *m*, H_2-8′), 2.05 (6H, *s*, OCOMe-9, 9′), 2.29 (3H, *s*, OCOMe-

4), 2.67 (2H, *t*, $J = 6$ Hz, H_2-7'), 3.80 (3H, *s*, OMe-3), 4.10 (2H, *t*, $J = 6$ Hz, $-CH_2OAc$-9'), 4.40 (2H, *m*, $-CH_2OAc$-9), 5.50 (1H, *d*, $J = 6.5$ Hz, H-7), 6.52–7.15 (6-ArH).

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6-*C*-GLUCOSYLNARINGENIN FROM FLOWERS OF *ACACIA RETINOIDE*

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Key Word Index—*Acacia retinoide*; Mimosaceae; 6-*C*-glucosylnaringenin; *C*-glycosylflavanone.

Abstract—From the flowers of *Acacia retinoide* 6-*C*-glucosylnaringenin has been identified.

C-Glycosylflavanones are rare plant constituents and only a few have been identified previously [1–5]. We now describe the characterization of 6-*C*-glucosylnaringenin (**1**) from the flowers of *Acacia retinoide*. This is the first report of a *C*-glycosylflavanone from the Mimosaceae.

1 showed colour reactions characteristic of a flavanone and its high R_f values in polar solvents and the results of the acid hydrolysis (extraction was possible with ethyl acetate or *n*-butanol but not with diethyl ether) suggested its *C*-glycosidic nature [6]. **1** had a UV spectrum and characteristic shifts of a flavanone with free hydroxyls in the C-5 and C-7 positions [7]. The mass spectrum of the PM derivative showed peaks at the following *m/z*: 546 $[M]^+$, 371 $[M-175]^+$ (100%) and a series of characteristic peaks of *C*-hexosides [8] with losses from the $[M]^+$ at -161, -189, -191, -205 and -218. In a study of the retro-Diels–Alder fragmentation with respect to the ions derived from the A ring, a series of significant peaks were found at the following *m/z*: 237, 223, 207, 193 and 179 corresponding to the ions *n*, *i*, *j*, $(j-2)$, *k* and *l* [9] of permethylated *C*-glycosidic flavones with methoxy substituents in the C-5 and C-7 positions. The characteristic peaks of the exposed ions, together with fragmentation proposed by Itagaki *et al.* [10], can be derived from two ions with distinct types of fragmentation: ion A_2^+ and/or A_1^+. With respect to the ions derived from B ring, we found B_3^+ and $[B_3-28]^+$ at *m/z* 161 and 133; and B_1^+ at *m/z* 134.

In view of these results **1** is shown to be a *C*-hexoside of a flavanone with the *C*-sugar in the 6- or 8-position with free hydroxyl groups at C-5 and C-7 and an oxygenated substituent on the B ring. Alkaline degradation gave *p*-hydroxybenzoic acid, identified by co-TLC with an authentic sample, which showed the presence of a hydroxyl group at the 4'-position. The production of a chalcone on permethylation of **1** made the location of the *C*-sugar by mass spectrometry impossible, and the difficulty of hydrolysing *C*-glycosides made it necessary to refer to the chromatographic evidence. Thus co-chromatography with an authentic sample in six chromatographic systems led to the conclusion that **1** was 6-*C*-glucosylnaringenin.

EXPERIMENTAL

Flowers of *Acacia retinoide* Schlecht (Mimosaceae), cultivated in gardens at Cabo Roig, Alicante, Spain, were gathered during May 1980 (No. 3733, voucher on deposit in the Herbarium of the University of Murcia, Spain). Plant material was extracted with Et_2O and EtOAc. The EtOAc