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Structures and Partial Syntheses of Machicendiol, Machicenonol and Machicenin—Three New Nor-Lignans from *Machilus glaucescens* : Preferred Conformation of the Side Chain of Machicendiol

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Three new nor-lignans, designated (−) machicendiol, machicenonol and machicenin have been isolated from the leaves of *Machilus glaucescens* Wight (fam. Lauraceae). Their structures have been determined as 2-(3, 4-methylenedioxy-phenyl)-5-(1, 3-dihydroxypropyl)-7-methoxybenzofuran (I), 2-(3, 4-methylenedioxyphenyl)-5-(1-keto-3-hydroxypropyl)-7-methoxybenzofuran (II) and 2-(3,4-dimethoxyphenyl)-5-(3-palmityloxypropyl)-7-methoxybenzofuran (III) respectively, largely based on their UV, PMR and mass spectral features. The structures have been confirmed by the unambiguous partial syntheses of (I) and (II) from egonol (IV) and that of (III) from homoegonol (V). Sesamin (VI), pinoresinol dimethyl ether (VII), (IV), (V) and β-sitosterol have also been isolated from this plant material. The preferred conformation of the 1, 3-dihydroxypropyl side chain of machicendiol has been suggested from the study of its 270 MHz PMR spectrum in $CDCl_3$.

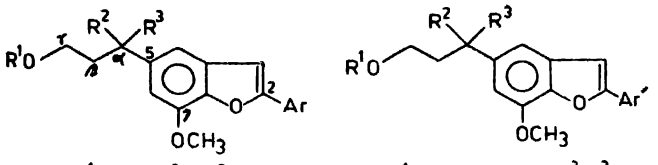
THE occurrence of varied types of secondary metabolites in some *Machilus* species (fam. Lauraceae), *viz.* benzyltetrahydroisoquinoline and aporphine alkaloids[1,2] from *M. arisanensis*, *M. zuihoensis*, *M. thunbergii* and *M. macrantha*, mono-and sesquiterpenes[3] from *M. japonica* and *M. thunbergii* and lignans From *M. edulis*[4] interested the present authors to undertake the chemical investigation on the virgin species of *Machilus glaucescens* Wight. The bark of *M. glaucescens* is used in the treatment of asthma, consumption and rheumation and the leaves are applied to ulcers[5].

Isolation of three new nor-lignans, machicendiol (I), machicenonol (II) and machicenin (III) from the leaves of this plant, and their structural elucidation, partial syntheses and the preferred conformation of the three-carbon side chain of (I) constitute the subject-matter of the present paper.

The dried and powdered leaves of *M. glaucescens* collected in Darjeeling district were extracted with light petrol (60-80°) and $CHCl_3$ in succession. The $CHCl_3$ extract upon exhaustive chromatography over silica gel and alumina yielded three new crystalline nor-lignans, machicendiol (I) (0.012%), machicenonol (II) (0.004%) and machicenin (III) (0.004%). Some known nor-lignans, egonol (IV) (0.005%) and homoegonol (V) (0.005%) and lignans sesamin (VI)[6] (0.003%), pinoresinol dimethyl ether (VII)[7] (0.008%) were obtained from the earlier eluate fractions. The petrol extract upon similar treatment yielded β-sitosterol and further amounts of sesamin (0.01%), egonol (0.015%) and homoegonol (0.01%).

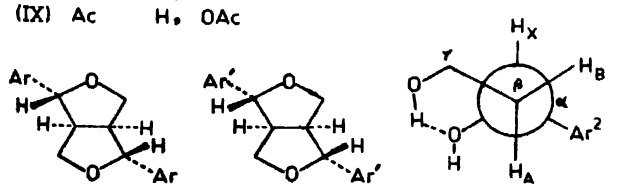
The isolation of machicendiol from *M. glaucescens* and the elucidation of its structure as 2-(3,4-methylenedioxyphenyl)-5-(1, 3-dihydroxypropyl)-7-methoxybenzofuran (I) on the basis of spectral (UV, IR and PMR) evidence were already reported from this laboratory in a preliminary communication[8]. Its structure was finally established by its three-step synthesis from the congener nor-lignan egonol (IV) as follows. Benzylic monobromination of (IV) with NBS in CCl_4 under reflux gave (VIII) (30%) which upon acetolysis with AgOAc in AcOH in presence of trace amount of Ac_2O afforded (±)-machicendiol diacetate (IX) (40%). The latter upon hydrolysis formed (±)-machicendiol (I) (80%). Both (±) (I) and (±) (IX) showed undepressed m.m.ps with the corresponding natural (−)-varieties thus indicating the formation of racemic solid solutions[9] in which a random arrangement of (±) and (−)-molecules occurred as a result of little difference in affinity between molecules of like and opposite configurations.

The 1,3-dihydroxypropyl side chain of (I) is expected to have a preferred conformation with the 1-aryl and 2-CH_2OH groups conformationally *anti* (eliminating the gauche interaction between them), an extra stability being caused by an intramolecular H-bonding of the 1,3-diol system (as already evident from its IR spectrum (3300 cm^{-1})[8]. The 270 MHz PMR spectrum of (I) in $CDCl_3$ (where H-bonding with the solvent does not occur and which is more revealing) supported the preferred conformation of the side chain as shown in the Newman projection formula (Ia). The spectrum clearly showed the X part of the ABX system Ar^2-CH_XOH-CH_AH_B-CH_2OH. The β-protons (H_A and H_B) being adjacent to the chiral centre (C-α) and free rotation being hindered due to intramolecular H-bonding, are diastereotopic and hence non-equivalent. H_X (H-α) appeared at δ 4.75 as a double doublet, J_{AX} = 9.5 Hz and J_{BX} = 4.5 Hz corresponding to the dihedral angles[10] $\phi_{H_A\text{-}H_X} \approx 180°$ and $\phi_{H_B\text{-}H_X} \approx 50°$. The coup-



	R^1	R^2, R^3
(I)	H	H, OH
(II)	H	O
(IV)	H	H, H
(VIII)	H	H, Br
(IX)	Ac	H, OAc

	R^1	R^2, R^3
(III)	$COC_{15}H_{31}$(n)	H, H
(V)	H	H, H

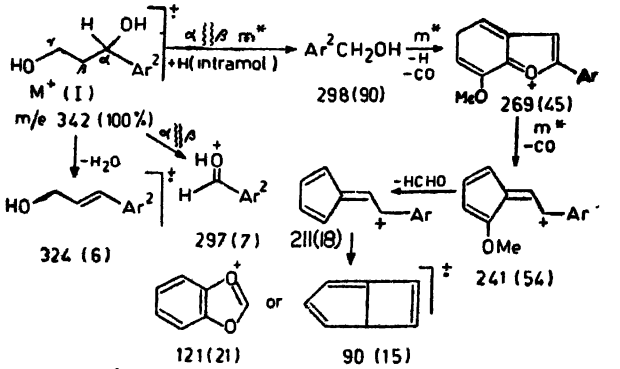


(VI) (VII) (Ia)

Ar=3,4-Methylenedioxyphenyl Ar'=3,4-Dimethoxyphenyl

Ar^2 = Benzofuran moiety of (I) or (II)

ling constants might have been affected to a certain extent by the electronegativity of the environment[10] (C-α being attached to Ar^2 and OH and C-β carrying CH_2OH). H_A and H_B exhibited appreciably different chemical shifts and appeared as a complex multiplet (δ 1.92-2.18) arising from a partial overlapping of a pair of 8-12 line multiplets [due to H_A-H_B(gem), H_A-H_X, H_A-$H_2(\gamma)$, H_B-H_X and H_B-H_2 (γ) interactions] the lower field multiplet ($\sim\delta$ 2.10) with greater separation of component lines [due to greater $J_{A\text{-}X}$ and $J_{A\text{-}H_2(\gamma)}$.] is assigned to H_A and the other multiplet at $\sim\delta$ 2.01 is due to H_B. The greater chemical shift value is also consistent with its proximity to α-OH.



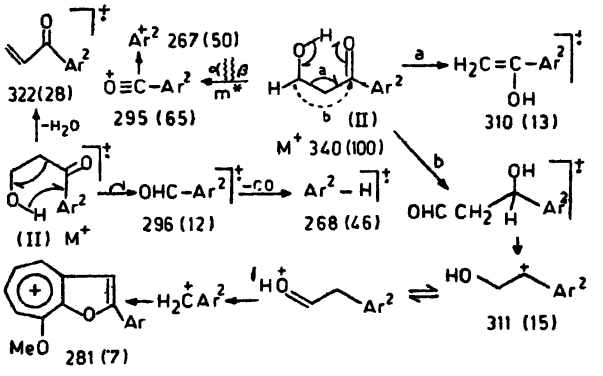
Ar^2 = Benzofuran moiety of (I) or (II)

Scheme. 1 Mass Fragmentation of Machicendiol (I)

The second new nor-lignan machicenonol (II), $C_{19}H_{16}O_6$, M^+ 340, showed bands for OH and conjugated CO groups in its IR spectrum. Its UV spectrum [λ_{max} 233 nm (log ϵ, 4.30), 283 (4.42) and 315(4.39)] was reminiscent of that of eupomatenoid-10, an isolate of *Eupomatia laurina*, having a 5-aldehydo-2-aryl benzofuran chromophore[11]. The 90 MHz (Perkin-Elmer R-32) PMR spectrum of machicenonol in $CDCl_3$ revealed all its structural features. The signals at δ 7.75 and 7.45 (1H *d* each, J_{4-6} = 2 Hz, H-4 and H-6), 6.92 (1H, *s*, H-3) and 4.03 (3H, *s*, OCH_3) were assigned to the 7-methoxy-2, 5-disubstituted benzofuran protons. The presence of the 3', 4'-methylenedioxyphenyl moiety was recognised by the signals at δ 6.85 (1H, *d*, $J_{5'-6}$ = 5 Hz, H-5'), 7.45 (1H, *d*, $J_{2'-6}$ = 2 Hz, H-2'), 7,32 (1H, *dd*, $J_{5'-6'}$ = 5 Hz, $J_{2'-6'}$ = 2 Hz, H-6') and 6.00 (2H, *s*, $-OCH_2O-$). The protons of the $C_3H_5O_2$ side chain at C-5 gave rise to the remaining signals at δ 4.02 (2H, *t*, J = 5.5 Hz, $-CH_2-CH_2-OH$) and 3.27 (2H, *t*, J = 5.5 Hz, $-CH_2CH_2$ CO-) thus identifying the side chain as 1-keto-3-hydroxypropyl group.

The final support to this structure came from the elegant one step conversion of machicendiol to machicenonol in 50% yield by selective oxidation of the former with Fetizon reagent[12].

The eletron impact induced significant fragments in the 70 e.v. mass spectra of (I) and (II) were also fully consistent with their structures and are rationalised in Schemes 1 and 2 respectively. Like other 2-arylbenzofuran nor-lignans both (I) and (II) exhibited the molecular ion peak as the base peak. The main fragmentation pathway in the spectra of (I) and (II), as expected, involved the typical benzylic cleavage of the α-β bond in the side chain leading to the second most abundant peaks at *m/e* 295(65%) and 298(90%) respectively. Comparison of the above fragmentations as well as that of (III) (Scheme 3) reveals that their patterns depend

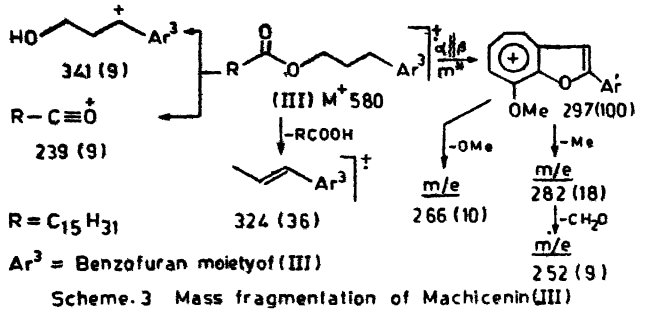


Scheme. 2 Mass fragmentation of Machicenonol (II)

upon the position and nature of the oxygenation in the side chain. It is interesting to note that the peak at *m/e* 281 (also found in the spectrum of egonol (IV) having no oxygen function at C-α) originated from the α-keto-γ-ol side chain (II) by a H migration ($\gamma \rightarrow \alpha$) followed by an OH migration ($\alpha \rightarrow \beta$) and subsequent benzylic cleavage, while the McLafferty rearrangement of the β-ketol system gave rise to the peak at *m/e* 310 (Scheme 2). The genesis of other significant fragments is outlined in the schemes (Schemes 1 and 2).

Machicenin (III), the third new nor-lignan, $C_{36}H_{52}O_6$, m.p. 94°, has been shown to have homoegonol palmitate (III). Its IR spectrum showed an ester CO stretching absorption at 1735 cm^{-1}. The UV spectrum was typical of a 2-arylbenzofuran system. The signals due to protons appearing downfield of δ 1.8 in its 100 MHz PMR spectrum were reminiscent of those

of homoegonol and a broad very intense high field peak was accountable for methylene protons of a fatty acid moiety. Thus the signals at δ 6.96 and 6.6 (1H *d* each, $J_{4-6}=2$ Hz, H-4 and H-6), 6.82 (1H, *s*, H-3) and 3.92 (3H, *s*, 7-OCH_3) were assigned to the 7-methoxy-2,5-disubstituted benzofuran protons of the homoegonol part. The presence of the 3',4'-dimethoxyphenyl moiety was recognised by the signals at δ 6.92 (1H, *d*, $J_{5'-6'}=7$ Hz, H-5'), 7.36 (1H, *d*, $J_{2'-6'}=2$ Hz, H-2'), 7.45 (1H, *dd*, $J_{5'-6'}=7$ Hz, $J_{2'-6'}=2$ Hz, H-6') 4.04 and 3.98 (3H *s*, each, 3'-OCH_3 and 4'-OCH_3). The protons of the side chain at C-5 gave rise to the remaining signals at δ 4.12 (2H, *t*, J=7 Hz, CH_2CH_2OCO-), 2.76 (2H, *t*, J=7 Hz, -CH_2CH_2Ar'), 2.32 (2H, *t*, J=7 Hz, -CH_2CH_2-COO), 2.00 [2H, *q*, OCH_2CH_2-CH_2Ar-the multiplicity(quintet) could be explained by splitting each component of a triplet, J=7 Hz, to individual overlapping triplets, J=7 Hz], 1.22–1.60 [26H, very srtong broad *s*, $(CH_2)_{13}$] and 0.90 (3H, *t*, J=6 Hz, CH_2CH_3). Thus the PMR data revealed the structure of machicenin as (III).



Scheme. 3 Mass fragmentation of Machicenin(III)

The significant peaks in the 70 e.v. mass spectrum of (III) are delineated in Scheme 3. The M^+ ion was not observed due to the ready cleavage of the ester moiety and the peak at *m/e* 341 (9%, $M^+ - COC_{15}H_{31}$) had the highest *m/e* value. However the M^+ at *m/e* 580 appeared as the base peak in its field desorption mass spectrum showing weak peaks at *m/e* 552, 524, 495, 410. The mass peaks in the electron impact spectrum of (III) after the typical elimination of the side chain leading to *m/e* 297 are similar to that of homoegonol (V).

Machicenin (III) on hydrolysis afforded homoegonol and palmitic acid (identified by GLC). Its structure was finally confirmed by its preparation by esterification of palmitic acid through its acid chloride with homoegonol.

It may be biogenetically and chemotaxonomically significant that *Machilus glaucescens* is the first *Machilus* species known so far to elaborate nor-lignans and that unlike many other Lauraceae plants it is devoid of any alkaloid component.

Experimental

M. ps were determined in a H_2SO_4 bath and are uncorrected. IR spectra were taken in KBr phase with a Beckmann IR-20 instrument. $CHCl_3$ and EtOH were used as solvents for recording optical rotations and UV spectra respectively. PMR spctra were determined for $CDCl_3$ solutions (unless otherwise mentioned) with TMS as internal reference on a Varian HA 100D or Brucker 270 MHz instrument and the chemical shifts are expressed in δ (ppm) units. Mass spectra were run in an AEI MS9 spectrometer at 70 e.v. using direct insertion probe. Petrol refers to light petroleum, b.p. 60-80°. Silica gel (100–200 mesh) of Gouri Chemicals, Calcutta and silica gel G were used for column chromatography and TLC respectively. Analytical samples were dried in *vacuo* at 80° over P_2O_5 for 24 hrs.

Investigation on the leaves—Dried and powdered leaves (1.0 Kg) of *M. glaucescens* were soxhletted successively with petrol and $CHCl_3$ for 40 hr. each. The residues 'A' (15 g) and 'B' (20 g) of the petrol and $CHCl_3$ extracts respectively lacked any basic constituents (Dragendorff test negative) and were separately chromatographed over silica gel (400 g, in a column (50×6 cm) elution being carried out with solvents and solvent mixtures of increasing polarity. Fractions were collected in 250 ml portions and monitored by TLC.

Chromatography of the petrol extract residue 'A'

Isolation of sesamin (VI) : Benzene fractions (28-36) of the chromatography of the residue 'A' showing identical major spot in TLC [R_f 0.45, $CHCl_3$] were combined and evaporated. The orange-yellow gummy residue (0.3 g) was subjected to rechromatography over silica gel to yield sesamin (VI), crystallising from $CHCl_3$-petrol in colourless needles (0.1 g), m.p. 125° $C_{20}H_{18}O_6$ (M^+ 354), $[\alpha]_D$+60°; λ_{max} 228 nm (log ϵ 3.98) and 280 (3.52); ν_{max} 1600 cm^{-1}, 1495 (aromatic), 1055 (dihydrofurofuran), and 923 (-OCH_2O-); PMR : 3.06 (2H, *m*, H-1 and H-5), 3.86 (2H, *dd*, J=9, 3.5 Hz, H_a-4 and H_a-8), 4.24 (2H, *dd*, J=9, 7 Hz, H_e-4 and H_e-8), 4.72 (2H *d*, J=5 Hz, H-2 and 6), 5.94 (4H, *s*, two -OCH_2O-), 6.78-6.84 (6H aromatic); MS (*m/e*, %base peak) : 354 (5, M^+), 203(20), 161(45), 149(100), 135(50), 122(40), 103(35), 91(30).

Isolation of a fatty alcohol and β-sitosterol: Petrol-benzene (1:1) fractions (18-25) afforded a residue (R_f 0-8 g, benzene) which upon rechromatography gave an uncharacterised fatty alcohol, 0-5 g (flakes from petrol), m. p. 80°; 3490 cm^{-1}(OH). Benzene: $CHCl_3$ (1 : 1) fractions (45-60) of the main chromatogram afforded greenish gummy residue (0.5 g) showing a single spot (R_f 0.4, $CHCl_3$), which upon rechromatography yielded β-sitosterol as fine flakes (0.1 g), m.p. 139°, $[\alpha]_D$ −37°, 3305 cm^{-1}(OH); Liebermann Burchardt test positive for sterol.

Isolation of egonol (IV) : $CHCl_3$ fractions (66-82) showing identical spot (R_f 0.5, 5% MeOH in $CHCl_3$) furnished a light green gummy solid (0.90 g) which upon repeated chromatography over silica gel gave egonol (IV) crystallising from $CHCl_3$-petrol as colourless needles (0.15 g), m.p. 113°, $C_{12}C_{18}O_5$ (M^+ 326); λ_{max} 217 nm (logϵ, 4.52) and 317 (4.52); ν_{max} 3300-3200 cm^{-1} (OH), 1600, 1590 (aromatic), 1470 (substituted furan ring), 1230, 1145 (cyclic ether), 935 (-OCH_2O-) : PMR : 1.75 (1H, *s*, OH), 1.9 (2H, *m*, H_2-β), 2.75 (2H, *t*, J=

7.6 Hz, H_2-α), 3.67 (2H, *t*, J=6.3 Hz, H_2-γ), 3.99 (OCH_3), 5.93 -OCH_2O-), 6.61-7.36 (six Ar-H) ; MS *m/e*, % base peak) : 326 (42, M^+), 308(3', M^+ -H_2O), 282(100, M^+ -C_2H_4O), 267(5), 181(5), 141(7).

Isolation of homoegonol (V) : The dark green gummy mass (0.9 g) obtained from the $CHCl_3$: MeOH (95:5) fractions (87-93) showed a major spot (R_f 0.2, 5% MeOH in $CHCl_3$) and a minor spot of egonol. It was purified by repeated chromatography over silica gel to afford pure homoegonol (V), crystallising from EtOAc-petrol as colourless needles (0.15 g), $C_{20}H_{22}O_5$ (M^+ 342), m.p. 126°, λ_{max} 217 nm (log ϵ 4.38) and 313 (4.30) ; 3360-3270 cm^{-1}(OH) 1620, 1600 (aromatic), I450 (substituted furan ring), 1230, 1145 (cyclic ether). PMR: 1.70 (1H, *s*, OH), 1.92 (2H, *m*, H_2-β), 2.78 (2H, *t*, J=7.5 Hz, H_2-α), 3.70 (2H, *t*, J=6.5 Hz, H_2-γ), 3.91, 3.98, 4.06 [(OCH_3)$_3$], 6.61−7.36 (six Ar-H) ; MS (*m/e*, % base peak) : 3·2 (93, M^+), 324 (4, M^+ -H_2O), 298 (100, M^+ − C_2H_4O), 283(68), 253(50 , 149(55).

Chromatography of the Chloroform extract Residue 'B'

Isolation of β-sitosterol, sesamin, egonol, homoegonol : Early benzene fractions (10−14) and later benzene fractions (16−21) afforded after crystallisations from suitable solvents further quantities of β-sitosterol (0.03 g), sesamin (0.03 g) respectively. The benzene-$CHCl_3$ (1:1) fractions (27−36) yielded a greenish gummy solid (1.3 g) showing two spots (R_f 0.5 and 0.3, 5% MeOH in $CHCl_3$) in TLC. The material was repeatedly chromatographed until complete separation was effected to yield further amounts of egonol (0.05 g) and homoegonol (0.05 g).

Isolation of pinoresinol dimethyl ether (VII) : The residue (0.8 g) of the early $CHCl_3$ fractions (41−46) showing a single spot (R_f 0·2, 5% MeOH in $CHCl_3$) upon rechromatography over silica gel afforded pinoresinol dimethyl ether, crystallising from $CHCl_3$-petrol as colourless flakes (0.08 g), m.p. 96.5°, $C_{22}H_{26}O_6$ (M^+ 386), $[\alpha]_D$+68°. Its UV, IR, PMR and MS data were identical with those reported earlier[13].

Isolation of machicendiol (I) : Later $CHCl_3$ fractions (47-52) showing in TLC a major spot [R_f 0.5, $CHCl_3$-MeOH (9:1)] furnished a brown gummy solid (0.8 g) which on chromatography successively over silica gel and alumina yielded machicendiol (I), crystallising from EtOAc-petrol as colourless flakes (0.06 g), m.p. 127°, $[\alpha]_D$−10° ; λ_{max} 218 nm (log ϵ 4.30) and 318 (4.56) ; ν_{max} 3300 cm^{-1} (H bonded OH), 1610 and 1590 (aromatic), 2900 (aliphatic C-H), 1470 (substituted furan ring), 1250, 1140 (cyclic ether), 930 (methylenedioxy) ; PMR (100 MHz, CD_3SOCD_3) : 1.80 (2H, *q*, J=6 Hz, H_2-β), 3.30-3.60 overlapped by DMSO signals (2H, *m* on D_2O exchange collapsing into a triplet, J=6 Hz, H_2−γ), 3.96 (3H, *s*, OCH_3), 4.44 (1H, *t*, J=5 Hz) disappearing on D_2O exchange, CH_2OH), 4.75 (1H, *m*, collapsing into a triplet on D_2O exchange, J=6 Hz, >C*H*OH), 5.18 (1H, *d*, J=6 Hz, >CHO*H*), 6.08 2H, *s*, =OCH_2O-), 6.9 and 7.23 (1H *d* each, J_{4-6}=2 Hz, H-4 and H-6), 7.12 (1H, *s*, H-3), 702 (1H, *d*, $J_{5'-6'}$= 6Hz, H-5'),7.43 (1H, *d*, $J_{2'-6'}$=2 Hz,H-2'), 7.40 (1H, *dd*, $J_{5'-6'}$=6 Hz, $J_{2'-6'}$=2 Hz, H-6') ; PMR (270 MHz, $CDCl_3$) : 1.92-2.18 (2H, *m*, H_2-β), 3.96 2H, *m*, H_2-γ), 4.05 (3H, *s*, OCH_3), 5.01 (1H, *dd*, J=9.5, 4.5, H-α), 6.01 (2H, *s*, -OCH_2-O-), 6,78 and 7.1 (1H, d each, J_{4-6}=2 Hz), 6.81 (1H, *s*, H-3), 6.86 (1H, *d*, $J_{5'-6'}$= 9 Hz, H-5'), 7.31 (1H, *d*, $J_{2'-6'}$=2 Hz, H−2'), 7,40 (1H, *dd*, $J_{6'-5'}$=9 Hz and $J_{6'-2'}$= 2Hz, H-6') ; MS : *m/e* (% base peak) : 342 (M^+, 100), 324(6), 311(2), 298(90), 283(13), 269(45), 254(8), 241(54), 211(18), 183(13), 121(12/. 90(15) (Scheme 1) (Found: C, 66.45 ; H, 5.00. Calc. for $C_{19}H_{18}O_6$ C, 66.66 ; H, 5.26%).

Isolation of machicenonol (II) : Earlier $CHCl_3$-MeOH (95:5) fractions (57-65) showed two spots R_f 0.45 and 0.5, $CHCl_3$-MeOH 9:1) along with an intense band due to gum which could be removed by rechromatography of the rasidue over silica gel. Repeated chromatography over alumina gave a further amount (0-02 g) of (I) (R_f 0.5) and a white solid (R_f 0.45 major, 0.5 minor). The latter on fractional crystallisation from hot $CHCl_3$ yielded the less soluble machicenonol, purified by recrystallisation, as colourless needles (0.2 g); m.p. 175°. ν_{max} 3440 cm^{-1} (O-H), 1675 (aryl CO), 1600, 1590 (aromatic), 1470 (substituted furan), 1250, 1150 (cyclic ether), 930 (methylenedioxy) ; MS; *m/e* (% base peak) : 340 (M^+, 100), 322(28), 311(15), 310(13), 296(12), 295(64), 281(7), 268(46), 267(50), 196(8), 147 (15) (Scheme 2) ; (Found C, 67.20 ; H, 4.50. Calc. for $C_{19}H_{16}O_6$: C, 67.00 ; H, 4.6%).

Isolation of machicenin (III) : Later $CHCl_3$-MeOH (95:5) fractions (66-70) showing a single spot (R_f 0.45, $CHCl_3$-MeOH, 95:5) furnished a greenish residue (0.2 g). This was purified by successive chromatographies over silica gel and alumina and finally by crystallising from $CHCl_3$-MeOH as colourless flakes 0-04 g), m.p. 94°, ν_{max} 2930 and 2860 (aliphatic C-H), 1735 (ester CO), 1615 and 1605 (aromatic), 1475 (substituted furan), 1270, 1220, 1170, 1145 (cyclic ether) ; MS: *m/e* (% base peak) : 341(9), 324(36), 310(15), 297(100), 282(18), 266(10), 261(21), 252(9), 239(9) (Scheme 3) ; field desorption MS: *m/e* (% base peak) 580 (M^+, 100), 552 (5, M^+ -$(CH_2)_2$), 524 (4, M^+-$(CH_2)_4$), 495(6, M^+ − $(CH_2)_5$-CH_3), 410(8, 495-$(CH_2)_5CH_3$),297(13, M^+ − RCOOCH$_2$-CH_2 CH_3), 296 (12, M^+ − $RCOOCH_2CH_3$).

Machicendiol diacetate (IX) : Machicendiol (0.015 g) was added to pyridine (0.5 ml) and Ac_2O (1 ml) and the mixture after keeping for 12 hr (R. T.) was poured into water (5 ml) Dil HCl was added till the solution was just acidic. It was then extracted with $CHCl_2$; the $CHCl_3$ layer was dried and evaporated. The residue was crytallised from petrol-MeOH as colourless filakes (0.01 g), m.p. 100°, $C_{23}H_{22}O_8$ (M^+ 426) ; ν_{max} 1735 cm^{-1} and 1720 (two $OCOCH_3$; s), 1615, 1590 (aromatic), 1470, 1350, 1220, 1140, 1100, 1020, 935, 920.

Hydrolysis ef machicenin (III) : Machicenin (III) (0.01 g) was refluxed with 5% methanolic KOH (5 ml)

for 35 min. on a water bath. The reaction mixture was cooled, diluted with water (10 ml), neutralised with 1N HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with $NaHCO_3$ solution and water, dried over anhydrous Na_2SO_4. The residue on evaporation gave homoegonol as colourless needles (from $CHCl_3$-petrol), m.p. 126°, identical with an authentic sample (m.m.p , co-TLC and superimposable IR).

Preparation of machicenin (III) *from homoegonol and palmitic acid* : A mixture of palmitic acid (0.02 g) and freshly distilled $SOCl_2$ (1 ml) was reflued for 0.5 hr, cooled and excess $SOCl_2$ was removed under vacuum. Homoegonol (0.016 g) was then added to a dry benzene (1 ml) solution of the resulting palmitoyl chloride. The mixture was refluxed for 0.5 hr. Benzene was removed and the residue was purified by chromatography. The white solid, thus obtained, on crystallisation from $CHCl_3$-MeOH afforded colourless flakes (0.01 g), m.p. 92°, identical (m.m.p., co-TLC and superimposable IR) with machicenin.

Preparation of α bromoegonol (VIII) : To a solution of egonol (0.1 g) in CCl_4 (10 ml), N-bromosuccinimide (0.060 g) and a few crystals of benzoyl peroxide were added to the mixture was slowly heated to boiling (80°) on a water bath for few min. It was shaken slowly for 0.5 hr without further heating. The succinimide formed floated on the surface of the liquid and was filtered off. The yellow solid residue obtained on evaporation in *vacuo* was chromatographed and crystallised from $CHCl_3$-petrol in light yellow needles (0.05 g), m.p. 163°, $C_{19}H_{17}O_5Br$ (M^+ 406) ; λ_{max} 318 nm (log ε 4.20) ; PMR: 2.05 − 1.98 (2H, *m*, H_2-β), 3.87 (2H, *t*, J = 5.5 Hz, H_2-γ), 4.03 (3H, *s*, OCH_3), 5.0 (1H, *t*, J=5.5, H-α), 5.98 (-OCH_2O-), 6.77-7.43 (6H, aromatic) ; MS ; *m/e* (% base peak) : 406(90), 401(85), 362(100), 360(88), 346(20), 331(7), 324(12).

Acetolysis of α-bromoegonol (VIII) *to α-acetoxyegonol acetate (machicendiol diacetate)* (IX) : AgOAc (0.1 g) was stirred in glacial AcOH (3 ml) for 15 min. Ac_2O (1ml) and α-bromoegonol (0.3 g) were added and the mixture was stirred for about 12 hr at 100-110° (oil bath) to ensure complete reaction. The mixture was then cooled, filtered washed with hot benzene and the filtrate was distilled under reduced pressure. The residue was crystallised from MeOH-petrol in colourless flakes (0.01 g), m.p. 100°, $C_{28}H_{22}O_8$ (M^+ 426). It was identified as machicendiol diacetate (IX) by direct comparison (m.m.p., co-TLC, superimposable IR).

Hydrolysis of α-acetoxyegonol acetate (IX) *to α-hydroxy egonol (machicendiol)* (I) : The diacetate (0.01 g) was refluxed with 10% methanolic KOH solution (5 ml) for 2 hr on a water bath. The solution was cooled, diluted with water (10 ml), neutralised with 1N HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried and evaporated. The residue was crystallised from petrol-$CHCl_3$ to yield colourless needles of α-hydroxy egonol (0.005 g), m.p. 124°, identical with the naturally occurring macicendiol (m.m.p., co-TLC, superimposable IR).

Preparation of machicenonol (II) *by oxidation of machicendiol* (I) *by Fetizon reagent*[12] : *Preparation of Fetizon reagent* : Purified celite (1.5 g) was stirred in a solution of $AgNO_3$ (1.9 g) in distilled water (10 ml) and a solution of Na_2CO_3, 10 H_2O (1.5 g) in distilled water (15 ml) was gradually added to it. After stirring for 10 min, the yellow green precipitate was filtered and washed to neutrality with distilled water and then dried several hr in a rotary evaporator.

Oxidation process : The reagent (0.2 g) was suspended in a benzene solution (60 ml) of machicendiol (0 017 g). The mixture was refluxed for 4 hr. The solid was filtered, the filtrate on evaporation afforded a solid which was chromatographed to get a single compound (TLC) crystallising from hot $CHCl_3$ in needles (0.01 g), m.p. 175°, found to be identical with the natural machicenonol by direct comparison m.m p., co-TLC and superimposable IR).

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