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SYNTHESIS OF THOMASIC ACID

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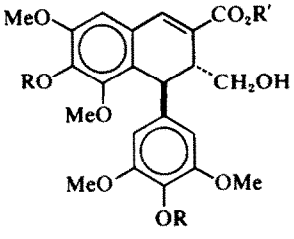
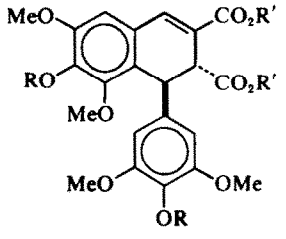
Abstract—Thomasidioic acid (**2**) has been synthesized in two steps by oxidative phenol coupling of sinapic acid (**6**) to the dilactone (**7**) followed by acid-catalyzed rearrangement. The diol dibenzyl ether (**15**), derived from thomasidioic acid dimethyl ester (**9**) by benzylation followed by LAH reduction, was selectively oxidized to yield thomasic acid (**1**) after debenzylation and base hydrolysis.

From aqueous extracts of the heartwood of *Ulmus thomasii Sarg.* ("rock elm"), Seikel *et al* isolated the novel lignans, thomasic acid (**1**) and thomasidioic acid (**2**) and established their structures by extensive spectroscopic and chemical degradation studies.[1,2] A significant contribution to the assignment of configuration was also made by Wallis.[3] Within the lignan class of natural products, these compounds display several unusual structural characteristics, (1) they are the only members known to date of the 1-aryl-1,2-dihydronaphthalene group, the only other naturally occurring aryldihydronaphthalene lignan, collinusin (**3**)[4,5] having a 1-aryl-3,4-dihydronaphthalene structure, (2) the presence of free carboxyl functionality in lignans is rare, plicatic acid (**4**)[6-8] from Western red cedar being apparently the only prior reported example, (3) their lack of optical activity might indicate a distinctive feature of biogenesis since all known naturally occurring aryltetralin lignans, for example, (with sole exception of (±)-lyoniresinol (**5**) which was also isolated from *U. thomasii*) are optically active, and (4) they provide interesting examples of a comparatively rare stereo-chemical situation in which *trans* vicinal substituents (at C-1,2) adopt diaxial conformations.[9,10] Naphthoic acid derivatives which are conceivably biodegradation products of thomasic acid have been isolated from the same source.[11] The heartwood extractives of other elm species have also been examined, prompted partly by the observation that the same phenolic substances which are extracted from the heartwood, although absent in the sapwood, are found in the "brown ring" area of the last annual growth rings symptomatic of Dutch elm disease.[12]

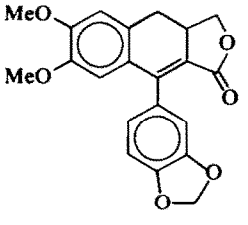
The synthesis of these two lignan acids (**1** and **2**) is the subject of this paper. Thomasidioic acid (**2**) was first synthesized in two steps from sinapic acid



1: R = R′ = H
13: R = R′ = Me
17: R = $CH_2C_6H_5$; R′ = Me
18: R = H; R′ = Me



2: R = R′ = H



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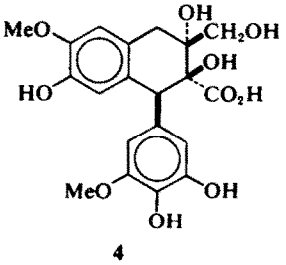

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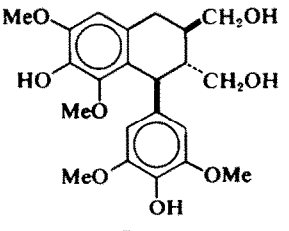

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(**6**); regiospecific manipulation of the C-3 allylic functionality then permitted the conversion of **2** to thomasic acid (**1**).

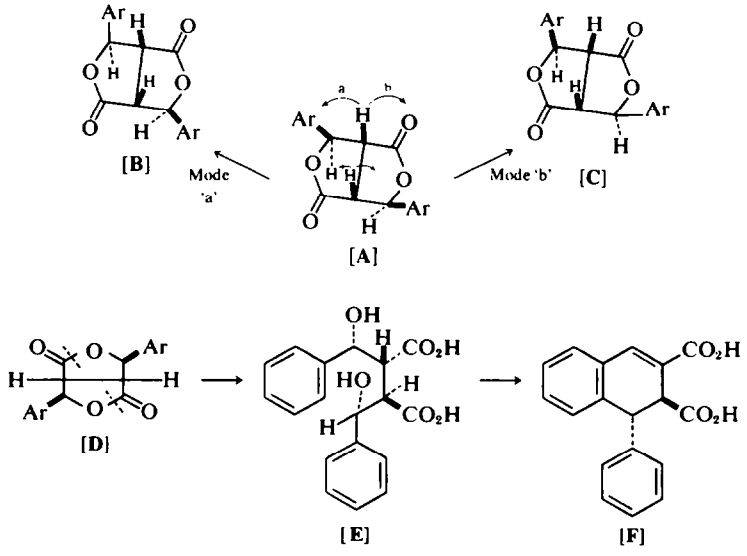
The oxidative coupling of ferulic acid (**19**) to yield "dehydrodiferulic acid" was first demonstrated by Erdtman,[13] and the dilactone structure of this product (**20**, without configuration assignment) established by Haworth.[14] The analogous oxidation of sinapic acid (**6**) to give "dehydrodisinapic acid dilactone" in 73% yield was later reported by Freudenberg.[15] As the first step in the synthesis, we have repeated the ferric chloride-oxygen coupling of sinapic acid. The γ-lactone functionality of the product is apparent in the IR spectrum and consideration of the NMR spectrum leads to the conclusion that the dilactone has the configuration of the thermodynamically most stable stereoisomer (**7**), with *cis* "diequatorial" aryl substituents. With strain considerations necessitating a *cis* fusion of the lactone rings, three substituent possibilities (two *cis* and one *trans* diaryl) exist. Since only one resonance signal is given for the benzylic proton (H-2,6) and one for the ring fusion proton (H-1,5), the *trans* diaryl isomer can be excluded. The small spin–spin coupling (J 1·5 Hz) shown by the H-1,5 protons is in agreement with that expected from the dihedral angle formed with the H-2,6 protons. In the model of the eclipsed conformation [**A**] the H(1)C(1)C(2)H(2) dihedral angle is 120° and a J value *ca* 4 Hz might be expected. A staggered conformation model [**B**] is realized by rotating apart the H_1 and H_5 protons in the sense 'a'. This has the effect of increasing the H(1)C(1)C(2)H(2) angle (and would presumably enhance J to *ca* 4-16 Hz) but introduces the destabilising feature of increasing the proximity of H-2 and H-6. The alternative staggered conformation [**C**]- by moving apart H-1 and H-5 in the sense 'b' is presumably more favorable since the H-2 and H-6 non-bonded interaction is decreased. In this conformation the H(1)C(1)C(2)H(2) dihedral angle is decreased (*ca* 90–120°) with a smaller J (0–4 Hz) expected. In the other *cis*-diaryl isomer, with aryl group *trans* to the H-1,5 proton ("diaxial"), the coupling constant for the H-1 and H-6 protons (dihedral angle *ca* 0°) should also be much larger.

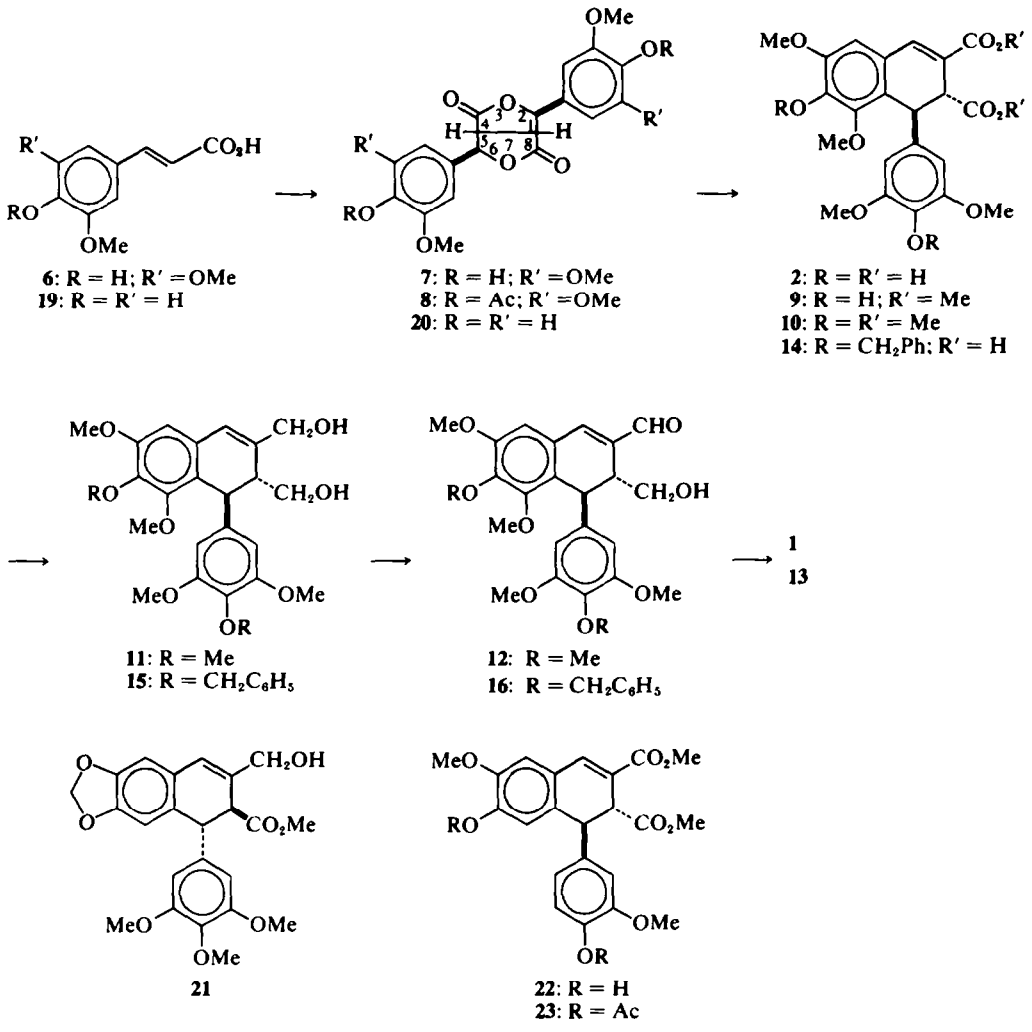
Since we found the melting point of **7** to be rather indefinite, the phenolic dilactone was further characterized as the diacetate (**8**) with m.p. in agreement with the previously reported value.[15]

With the relative configurations of the four asymmetric centres of **7** established, it was considered that intermediate [**E**] (or an equivalent) obtained by acidic hydrolysis of such a dilactone [**D**] would be well disposed for both dehydration and cyclization to yield the desired aryl *trans*-1,2-dihydronaphthalene system [**F**].

This was found to be the case and treatment of **7** with hydrochloric acid in aqueous dioxan gave thomasidioic acid (**2**) in excellent yield.[16] Alternatively, by heating a solution of the dilactone (**7**) in methanol saturated with hydrogen chloride, there was obtained in quantitative yield thomasidioic acid dimethyl ester (**9**). Both **2** and **9** were further characterized by methylation with diazomethane to yield the previously reported dimethyl ether dimethyl ester (**10**). A comparison of the IR and NMR spectra of **2** and **10** so obtained with authentic specimens confirmed their identity.

Completion of the synthesis of thomasic acid (**1**) requires a selective reduction of the C-2 carboxyl of thomasidioic acid (**2**) to a primary alcohol. The route chosen involved the reduction of both C-2 and C-3 carboxyl groups followed by a selective oxidation of the C-3 allylic primary alcohol function. To test the applicability of this plan, the synth-





esis of the known methyl thomasate dimethyl ether (**13**) was first undertaken. Accordingly, the dimethyl ester dimethyl ether (**10**) was reduced with LAH to give the diol (**11**) (absence of IR CO absorption) which on oxidation with active manganese dioxide[17] gave the conjugated aldehyde (**12**) (low field aldehyde proton in NMR spectrum and conjugated carbonyl in IR spectrum). The aldehyde function was then selectively oxidized in the presence of the C-2 primary alcohol function (Corey's method[18]) by manganese dioxide in methanol solution containing hydrogen cyanide to give methyl thomasate dimethyl ether (**13**). It was unnecessary to isolate and/or purify any of these intermediates, the essential completion of each step being ascertained by appropriate spectra determination.

To prepare thomasic acid by the same pathway, the phenol functions of dimethyl thomasidioate (**9**) were protected by benzylation to yield the dibenzyl ether dicarboxylic acid (**14**) which on LAH reduction gave the diol (**15**). The double manganese dioxide oxidation first to the aldehyde (**16**), then to the methyl ester (**17**) was followed by debenzylation by mild hydrogenolysis to give methyl thomasate (**18**), not previously described, but identical with a specimen prepared by methyl esterification of authentic thomasic acid. Base hydrolysis of **18** gave thomasic acid (**1**).

The NMR data for thomasic acid and synthetic intermediates are summarized in Table 1 and support the assigned structures. Thus, in $CDCl_3$ solution, the C-8 OMe group (with adjacent C-7 phenol or methyl ether function) is located in the range (δ 3·60–3·67) characteristic of shielding by an axial C-1 aryl group.[2,3] It is noted that this signal is further shielded (δ 3·53) by an adjacent benzyl group. The H-1 proton signal is typically a broadened singlet and the H-2 either a singlet or doublet of small coupling constant (J 1·5 Hz). Ayres, among his observations on spectroscopy and conformation of *apo*

Table 1. NMR data for thomasic and thomasidioic acid derivatives

Compound	Solvent	H-1	H-2	H-4	H-5	H-2′,6′	Methoxyl			-OMe	Signals		
							6	8	3′,5′	Observed	Present		Other
Thomasidioic acid (2)	$(CD_3)_2CO$	5·08 br.s.	4·02 d.(J1·5)	7·70	6·97	6·42	3·90	3·65	3·70	3	4		
Dimethyl ester (9)	$CDCl_3$	5·02 br.s.	4·03 d.(J1·5)	7·65	6·72	6·30	3·92	3·65	3·75	3	6	3·65 3·75	C-2 CO_2Me C-3 CO_2Me
Dimethyl ester dimethyl ether (10)	$CDCl_3$	5·00 br.s.	4·07 d.(J1·5)	7·65	6·73	6·28	3·89	3·67	3·73	4	8	3·67 3·78 3·78 3·89	C-2 CO_2Me C-3 CO_2Me 4′ OMe 7 OMe
Diol dimethyl ether (11)	$CDCl_3$	4·40 br.s.	[a]	6·46	6·55	6·32	3·85	3·60	3·72	5	6	3·78 3·88 4.1 br. 3.0 br.	4′ OMe 7 OMe C-3 CH_2OH C-2 CH_2OH
Aldehyde dimethyl ether (12)	$CDCl_3$	4·67 br.s.	3·85[b]	[a]	6·77	6·23	3·90	3·60	3·70	4	6	3·73 3·90 3·2–3·5 9.60	4′ OMe 7 OMe C-2 CH_2OH C-3 CHO
Methyl ester dimethyl ether (13)	$CDCl_3$	4·67 br.s.	[a]	7·60	6·72	6·30	3·92	3·62	3·73	4	7	3·80 3·80 3·92 *ca* 3·33 4·10	C-3 CO_2Me 4′ OMe 7 OMe C-2 CH_2OH C-3 CH_2OH
Methyl ester dimethyl ether (13)	$(CD_3)_2SO$	4·73 br.s.	[a]	7·62	7·10	6·28	3·87	3·58 (or 3·61)	3·65	6	7	3·61 (or 3·58) 3·71 3·81	OCH_3 groups
Dibenzyl ether dicarboxylic acid (14)	$CDCl_3$	[a]	4·02 br.s.	7·78	6·73	6·22	3·85	3·53	3·67	3	4	4·93 5·03 7·0–7·5 11.1	-CH_2Ph -CH_2Ph ArH -CO_2H
Dibenzyl ether diol (15)	$CDCl_3$	4·42	[a]	6·43	6·53	6·30	3·82	3·53	3·63	3	4	4·97 5·03 7·1–7·5 4·02	-CH_2Ph -CH_2Ph ArH C-3 CH_2OH
Dibenzyl ether aldehyde (16)	$COCl_3$	4·68 d(J3·5)	[a]	[a]	6·77	6·23	3·87	3·53	3·67	3	4	4·95 5·08 7·2–7·6 9·58 *ca* 3·3	-CH_2Ph -CH_2Ph ArH -CHO C-2 CH_2OH
Methyl thomasate dibenzyl ether (17)	$CDCl_3$	4·67 br.s.	[a]	7·60	6·70	6·27	3·87	3·53	3·68	4	5	3·75 4·97 5·07 7·2–7·6 *ca* 3·3	C-3 CO_2Me -CH_2Ph -CH_2Ph ArH C-2 CH_2OH

Methyl thomasate (**18**)	$CDCl_3$	4·65	[a]	7·60	6·70	6·30	3·93	3·60	3·77	3	5	3·77 *ca* 3·3	C-3 CO_2Me C-2 CH_2OH
Thomasic acid (**1**)	$(CD_3)_2CO$	4·87 br.	3·85[b]	7·62	6·93	6·40	3·92	3·62	3·70	3	4	*ca* 3·2	C-2 CH_2OH
Dimethyl ester (**22**)	$CDCl_3$	4·57 d(J3·5)	4·00 d(J3·5)	7·68			3·90		—	4	4	3·63 3·75 3·77 6·3–6·9	C-2 CO_2Me C-3′ OMe C-3 CO_2Me ArH
Dimethyl ester (**23**) diacetate	$CDCl_3$	4·67 d(J3·5)	4·05 d(J3·5)	7·68			3·83		—	4	4	3·62 3·70 3·77 2·23	C-2 CO_2Me C-3′ OMe C-3 CO_2Me C-7 and 4′ Acetates

[a]Indistinct, or hidden by other signal (-OMe, $ArCH_2$- or ArH).
[b]Partly hidden.

compounds of arylnaphthalene systems,[10] reproduced a 100 Hz spectrum of methyl α-apopicropodophyllate (**21**), a good stereochemical analogue of thomasic acid except for the absence of the C-8 OMe function, and noted a 4 Hz coupling for these H-1,2 diequatorial protons; that difference must reflect the increased steric repulsion of the C-1 and C-8 substituents. In agreement with this, we have prepared as previously described the dimethyl ester (**22**),[14] the thomasidioic acid dimethyl ester analogue lacking the C-8 (and C-5') OMe group, and its diacetate ester (**23**) and find that a 3·5 Hz coupling is found for the H-1 and H-2 protons.

EXPERIMENTAL

M.ps were determined with either a Gallenkamp or Fisher-Johns apparatus and are uncorrected. NMR spectra were determined for solns with TMS as internal reference on a Varian A60 spectrometer. IR spectra, unless otherwise stated, were determined in KBr pellets using a Perkin-Elmer Infracord spectrophotometer.

r-1H-2*c*,6*c*-*Bis* - (4' - *hydroxy* - 3',5' - *dimethoxyphenyl*) - 3,7 - *dioxabicyclo* - [3,3,0] - *octane* 4,8 - *dione*

"*Dehydrodisinapic acid dilactone*" (**7**). A rapid stream of O_2 was passed through a soln of $FeCl_3$ (20 g) in water (800 ml) during the addition of a soln of **6** (10 g) in MeOH (200 ml) over 10 min. A red-violet ppt immediately separated. The O_2 passage was continued for 5 h and the mixture allowed to stand overnight. The ppt was then collected as a paste, suspended in water (120 ml), heated for 10–15 min on steam bath and acidified with dil (1:1) H_2SO_4 (120 ml) with vigorous shaking. After cooling, the product was collected as a pink solid, washed with ether, and crystallized from acetone-MeOH to yield the dilactone as colourless prisms (6·5 g), m.p. 227–235° (darkening at 220°), (lit.[15] m.p. 208°); λ 2·97 (-OH) and 5·63 μ (lactone). NMR spectrum (hexadeuterioacetone): δ 3·85s. (12, -OMe groups), 3·94d. (J 1·5) (2, H-1 and 5), 5·77br.s. (2, H-2 and 6), 6·75s. (4, Ar-H) and 7·15–7·50 br. (2, Ar-OH).

r-1H-2*c*,6*c*-*Bis* - (4'-*acetoxy*-3',5' - *dimethoxyphenyl*)-3,7 - *dioxabicyclo* - [3,3,0] - *octane* - 4,8 - *dione*

"*Dehydrodisinapic acid dilactone diacetate*" (**8**). Ac_2O (5 ml) and pyridine (5 ml) were added to **7** (100 mg), the mixture warmed for 5 min and stirred overnight at room temp. The ppt produced on the addition of crushed ice was collected, dissolved in acetone (charcoal treatment) and crystallized from aqueous acetone as prisms (65 mg), m.p. 232–234° (lit.[15] m.p. 228–230°); λ 5·58 (lactone) and 5·65 μ (ester). NMR spectrum (hexadeuterioacetone) δ 2·23s. (6, -OAc), 3·85s. (12, -OMe groups), 4·20d. (J *ca* 1) (2, H-1 and 5), 5·88 br.s. (2, H-2 and 6) and 6·83s. (4, Ar-H).

7-*Hydroxy* - 6,8 - *dimethoxy* - 1-(4'-*hydroxy* - 3',5' - *dimethoxyphenyl*)-trans - 1,2-*dihydronaphthalene* - 2,3-*dicarboxylic acid*

"*Thomasidioic acid*" (**2**). Conc HCl (1 ml) was diluted with water (to 10 ml), and this soln (4 ml) added to a soln of **7** (50 mg) in dioxan (5 ml). The mixture was heated on the steam bath for 45 min and evaporated under reduced pressure until a ppt appeared. This was collected (45 mg), dissolved in NaOHaq and reprecipitated by acid neutralization. Two "crystallizations" from acetone-chloroform gave thomasidioic acid as a white solid of indefinite m.p. (typically decomposing *ca* 210° and completely liquified *ca* 250°), λ 5·88 (C-2 carboxyl) and 5·92 μ (C-3 carboxyl).

Dimethyl 7-*hydroxy*-6,8-*dimethoxy*-1-(4'-*hydroxy*-3',5'-*dimethoxyphenyl*)-trans-1-, 2-*dihydronaphthalene*-2,3-*dicarboxylate*

"*Thomasidioic acid dimethyl ester*" (**9**). MeOH (15 ml) saturated with HCl was added to **7** (500 mg) and the mixture heated under reflux for 2 h. Within the first 30 min, it successively turned yellow, pale green, dark green and then decolorized. Addition of water yielded a solid (500 mg) which on crystallization from aqueous MeOH gave **9** as plates, m.p. 201–203°, λ 2·89 (-OH), 5·78 (C-2 ester) and 5·88 μ (C-3 ester). (Found: C, 60·72, H, 5·31. $C_{24}H_{26}O_{10}$ requires: C, 60·75; H, 5·52%).

Dimethyl 6,7,8-*trimethoxy*-1-(3',4',5'-*trimethoxy*-*phenyl*)-trans-1,2-*dihydronaphthalene*-2,3-*dicarboxylate*

"*Thomasidioic acid dimethyl ester dimethyl ether*" (**10**). (a) Excess diazomethane in ether was added to a soln of **9** (80 mg) in acetone (10 ml), stirred at 0° for 4 h and at room temp overnight. The product, after solvent evaporation, was chromatographed on silica gel PF [1 mm, benzene–acetone (4:1)]. Crystallization from aqueous MeOH gave the dimethyl ester dimethyl ether as rosettes of needles (50 mg), m.p. 121–122°. (Lit.[2] m.p. 142·5–143°). Seeding of an aqueous methanolic soln with an authentic higher melting form gave prismatic needles, m.p. and mixed m.p. 143–143·5°. The higher melting form was also obtained by crystallization from aqueous acetone. λ 5·76 (C-2 ester) and 5·86 μ (C-3 ester). A comparison of the IR and NMR spectra of the synthetic and natural derivatives established their identity.

(b) A soln of **2** (55 mg) in MeOH (10 ml) was similarly methylated. One crystallization of the product from aqueous acetone gave **10** (25 mg), m.p. 117–118°.

Conversion of thomasidioic acid dimethyl ester dimethyl ether (**10**) *to thomasic acid methyl ester dimethyl ether* (**13**)

A soln of **10** (200 mg) in ether (75 ml) was added to LAH (200 mg) in ether (100 ml) at 0°. The mixture was stirred for 1 h, then worked up in the usual way to give an oil (180 mg) which deposited the diol (**11**) as a solid (120 mg), m.p. 125–126° (absence of CO absorption in IR spectrum; see chart for NMR data). (Found: C, 64·79; H, 6·59. $C_{24}H_{30}O_8$ requires: C, 64·56; H, 6·77%). The crude diol (200 mg) in ether (15 ml) and hexane (5 ml) was added dropwise to a suspension of MnO_2 (1 g) in ether (15 ml) at 0°, the mixture stirred for 1 h, filtered and evaporated to give an oil, considered to be the *aldehyde*, **12** (λ 2·95 (-OH) and 5·95 μ aldehyde; see chart for NMR data). This oil was dissolved in MeOH (15 ml), and NaCN (60 mg), acetic acid (few drops) and MnO_2 (1·2 g) added. The mixture was stirred overnight at room temp, filtered, evaporated and the residue partitioned with water and ether. Evaporation of the dried ether extract gave a solid residue (135 mg) which crystallized from ether-light petroleum to yield *methyl* 6, 7, 8 - *trimethoxy* - 1 - (3', 4', 5' - *trimethoxyphenyl*) - 2 - *hydroxymethyl* - trans - 1, 2 - *dihydronaphthalene* - 3 - *carboxylate* (**13**) ("methyl thomasate dimethyl ether") as small needles (55 mg), m.p. 118–120° (lit.[1] m.p. 121·5–122·5°), λ 2·88 (-OH) and 5·86 μ (ester).

Conversion of thomasidioic acid dimethyl ester (**9**) *to thomasic acid* (**1**).

(a) *Formation of dibenzyl ether dicarboxylic acid* (**14**). Freshly distilled benzyl chloride (40 mg) and **9** (100 mg) were added to a soln of KOH (150 mg) in water (1 ml), the mixture heated under reflux for 5 h, cooled, diluted with water and extracted with ether. Acidification of the aqueous phase with dil HCl precipitated **14** as an oily solid (120 mg); NMR spectrum (see chart).

(b) *Formation of dibenzyl ether diol* (**15**). A soln of **14** (400 mg) in ether (20 ml) was added to a suspension of LAH (300 mg) in the same solvent (15 ml) at 0°. The mixture was stirred at 0° for 2 h then for a further 1 h at room temp. Work up in the usual way gave the *diol* (**15**) as a solid (220 mg), λ ($CHCl_3$) 5·85 μ (double bond); NMR spectrum (see chart).

(c) *Formation of dibenzyl ether aldehyde* (**16**). A soln of **15** (150 mg) in ether (12 ml) and hexane (4 ml) was stirred with MnO_2 at 0° for 30 min. Evaporation of the solvent after filtration yielded **16** as a yellow oil (130 mg), λ ($CHCl_3$) 6·00 μ (conjugated carbonyl); NMR spectrum (see chart).

(d) *Formation of methyl thomasate dibenzyl ether* (**17**). A mixture of **16** (100 mg), NaCN (160 mg), AcOH (60 mg) and MnO_2 (1·1 g) in MeOH (20 ml) was stirred overnight at room temp, filtered and evaporated. The residue was partitioned between water and ether, and the dried ether extract evaporated to give the *methyl ester* (**17**) as a yellow oil (100 mg), λ ($CHCl_3$) 5·91 μ (conjugated ester); NMR spectrum (see chart).

(e) *Formation of methyl thomasate* (**18**). A soln of **17** (100 mg) in AcOH (20 ml) was stirred with 10% Pd-C (100 mg) under a H_2 atmosphere (slightly reduced pressure) for 8–11 min (no further observed H_2 uptake). Methyl thomasate, (**18**) was obtained, after filtration and solvent removal, as a yellow oil (90 mg), identified by comparison of IR and NMR spectra of authentic specimen prepared by methyl esterification of natural thomasic acid.

(f) *Formation of thomasic acid* (**1**). 2N KOH (5 ml) was added to a soln of the crude methyl ester (oil, 90 mg) in MeOH (5 ml), the mixture heated under reflux for 2 h, cooled, acidified with dil HCl and extracted with ether to yield the product as a yellow oil (60 mg). Several crystallizations from water yielded **1** as prisms, m.p. and mixed m.p. 238–239° (after drying *in vacuo* over P_2O_5 at 100°). (Lit.[1] m.p. 232–234°); NMR spectrum (see chart).

Methyl 7-hydroxy-6,8-dimethoxy-1-(4'-hydroxy-3',5'-dimethoxyphenyl)-2-hydroxymethyl-trans-1,2-dihydronaphthalene-3-carboxylate

"*Methyl Thomasate*" (**18**). Conc HCl (1 ml) was added to a soln of thomasic acid (50 mg, isolated from *U. thomasii*), the mixture heated under reflux for 2 h, concentrated, diluted with water and extracted with chloroform. Evaporation of the dried extract gave a red oil which was crystallized from aqueous MeOH to give *methyl thomasate* as "off-white" needles, m.p. 229°, λ 5·96 (ester) (Found: C, 61·61; H, 6·11. $C_{23}H_{26}O_9$ requires: C, 61·87; H, 5·87%).

r-1H-2c, 6c-Bis-4'-hydroxy-3'-methoxyphenyl)-3, 7-dioxabicyclo-[3,3,0]-octane-4,8-dione

"*Dehydrodiferulic acid dilactone*" (**20**). Prepared from **19** as previously described, had m.p. 207–211° (lit.[14] m.p. 208–209°), λ 5·57 μ (lactone). NMR spectrum (hexadeuterioacetone): δ 3·87s, (6, OMe groups), 4·08d. (J = 1 Hz) (2, H-1 and 5), 5·80d. (J = 1 Hz) (2, H-2 and 6) and 6·88–7·13 m. (6, ArH).

Dimethyl 7-hydroxy-6-methoxy-1-(4'-hydroxy-3'-methoxyphenyl)-trans-1,2-dihydronaphthalene-2,3-dicarboxylate, (**22**). Prepared as previously described, had m.p. 205–208° (lit.[14] m.p. 203–205°), λ 5·77 and 5·91 μ (esters); NMR spectrum (see chart). Treatment with pyridine and Ac_2O in the usual way gave the diacetate (**23**) as fine needles, m.p. 199–201° on crystallization from chloroform-MeOH.

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