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SYNTHESIS OF CLAUSENIN, XANTHOXYLETIN, ALLOXANTHOXYLETIN, XANTHYLETIN AND NOR-DALBERGIN*

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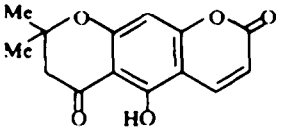
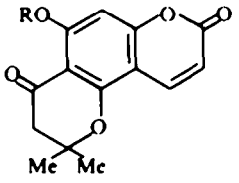
Abstract– The synthesis of clausenin is reported. Clausenin on methylation, $NaBH_4$ reduction and dehydration of the secondary alcohol gives xanthoxyletin. The angular isomer of clausenin by a similar series of reactions gives alloxanthoxyletin. A convenient synthesis of xanthyletin and nor-dalbergin has also been achieved.

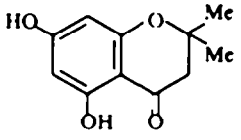
IN THE preceding paper[1] we described the isolation of clausenin from the roots of *Clausena heptaphylla* wt. & Arn. and proposed the structure I or IIa on the basis of spectral and degradative evidence. In this paper we report an unambiguous synthesis of I. 5,7-Dihydroxy-2,2-dimethyl chroman-4-one (III),[2] prepared from phloroglucinol and α,α-dimethyl allylchloride was condensed with ethyl propiolate in presence of zinc chloride.[3] This gave a mixture of two isomeric compounds $C_{15}H_{12}O_5$ which were separated by chromatography on silica gel. The slower moving compound (A) had m.p. 156–157° and the faster eluted product (B) melted at 220°. Theoretically, three pyrano coumarins (I, IIa and IV) could be formed in this reaction. Since both the isolated compounds (A and B) showed chelated carbonyl



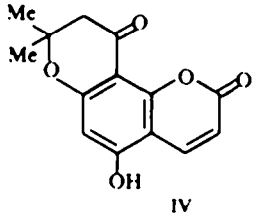
I



IIa: R = H
b: R = Me



III



IV

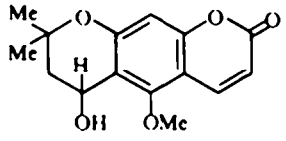
III + CH≡C·COOEt → A (m.p. 156°) + B (m.p. 220°)

* Contribution No. 93 from CIBA Research Centre.

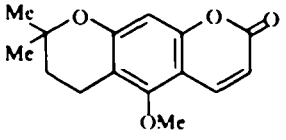
[1] B. S. Joshi, V. N. Kamat and A. K. Saksena, *Tetrahedron* to be published (1968).
[2] W. Bridge, R. G. Heyes and A. Robertson, *J. Chem. Soc.* 279 (1937).
[3] K. D. Kaufman and R. C. Kelly, *J. Heterocyclic Chem.* 2, 91 (1965).

peaks in their IR spectrum, the structure IV was ruled out. However, on the basis of spectral evidence alone it is not possible to assign definite structures for the compounds A and B.

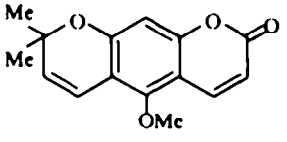
The compound A on methylation with diazomethane and reduction of the methyl ether with $NaBH_4$[4] gave a mixture of two products. Chromatographic separation on silica gel provided the secondary alcohol $C_{15}H_{16}O_5$ (V), m.p. 142°, and the corresponding deoxydihydro derivative (VI), m.p. 144°. The compound V on heating with potassium bisulphate gave the dehydration product m.p. 130°. This was found to be identical with a natural sample of xanthoxyletin in its mixed m.p., TLC behaviour, IR and NMR spectra. Since xanthoxyletin is proven to have the structure VII.[5] it follows that the product A should be assigned structure I and the product B



V



VI



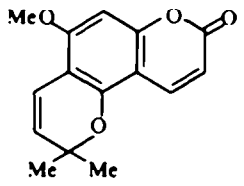
VII

should have the structure IIa. The synthetic compound A and its methyl ether were identical with clausenin and its methyl ether in their mixed m.p., TLC, IR and NMR spectra. Clausenin should therefore be constituted as 7,8-dihydro-8,8-dimethyl-5-hydroxy-6-oxo-pyrano-(2,3-g)-coumarin (I). NMR spectral evidence for the $NaBH_4$ reduction products was in support of the formulations V and VI. The *gem*-dimethyl groups of the compound V showed different chemical shifts at 1·4 and 1·48 δ. The angular isomer of clausenin (IIa) showed λ_{max} 218, 324 mμ (log ε, 4·49, 4·15) and IR bands at 1730, 1625, 1590 (coumarin), 1650 (chelated $\rangle C{=}O$) cm^{-1}. The NMR spectrum was almost similar to that of clausenin with a slight downfield shift of the aromatic proton at 6·36 δ. Methylation of IIa with diazomethane gave the corresponding methyl ether (IIb), m.p. 193–194°. The ketone carbonyl now appeared at 1691 cm^{-1}. Reduction of the methyl ether with $NaBH_4$ gave a mixture which could be separated by chromatography on silica gel. The secondary alcohol m.p. 135° was dehydrated by heating with potassium bisulphate. The resulting compound had m.p. 115–116° which is identical with the reported m.p. of alloxanthoxyletin (VIII)[6]. A direct comparison with natural alloxanthoxyletin could not be made due to nonavailability of a sample. The chroman (IX) obtained by Clemmenson reduction

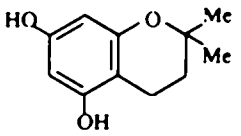
[4] J. Nickl, *Chem Ber* **92**, 1989 (1959).

[5] A. Robertson and T. S. Subramaniam, *J. Chem. Soc.* 286 (1937); H. Dieterle and E. Kruta, *Arch Pharm* **275**, 45 (1937).

[6] A. Robertson and T. S. Subramaniam, *J. Chem. Soc.* 1545 (1937).

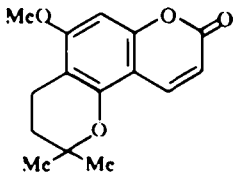


VIII

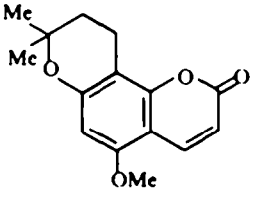


IX

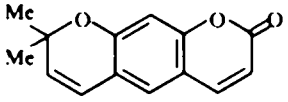
of II[2] when condensed with ethyl propiolate gave a mixture of two products. The mixture on methylation and chromatography on silica gel provided two isomeric compounds $C_{15}H_{16}O_4$. The slower moving fraction (R_f 0·64) had m.p. 153–155° which appears to be identical with the reported m.p. of dihydroalloxanthoxyletin (X; Lit. m.p. 153–155°). The mother liquor gave a compound m.p. 162° (R_f 0·73). Since this compound is not identical with dihydroxanthoxyletin (VI), it has been assigned the structure XI on the basis of analysis, IR and NMR spectra.



X

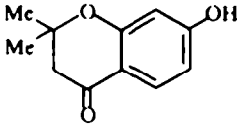


XI

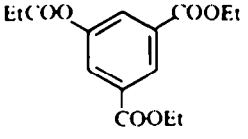


XII

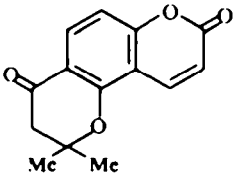
The preparation of the coumarins (I and IIa) from III led us to attempt the synthesis of xanthyletin[7] (XII) from 2,2-dimethyl-7-hydroxychroman-4-one (XIII). On heating XIII with ethyl propiolate in presence of anhydrous zinc chloride, trimesic acid triethylester (XIV) and another crystalline compound $C_{14}H_{12}O_4$ were obtained.



XIII



XIV

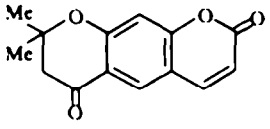


XV

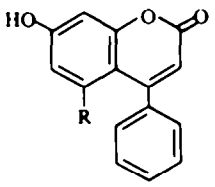
This has been assigned structured XV based on the following evidence. In the IR it showed peaks at 1740, 1730, 1620, 1600 (coumarin) and 1690 (α,β-unsaturated ketone) cm^{-1}. In the NMR it showed signals at 1·7 (6H, S, gem-dimethyl), 2·8 (2H, S, $-\overset{O}{\overset{\|}{C}}-CH_2-$), 6·41 (1H, d, J = 10 c s, C-3 proton of coumarin), 6·96 (1H, d, J = 10 c s), 8·06 (1H, d, J = 10 c s, C-4 proton of coumarin) and 8·12 δ (1H, d, J = 10 c s). The pair of doublets at 6·96 and 8·12 δ is due to C-9 and C-10 ortho protons. The linear structure XVI is thus ruled out on the basis of NMR spectrum. However,

[7] J. C. Bell and A. Robertson, *J. Chem. Soc.* 1828 (1936); E. Späth and R. Hillel, *Ber. Dtsch. Chem. Ges.* 72, 2093 (1939).

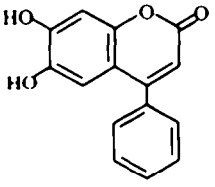
xanthyletin was synthesized from dihydroxanthyletin[8] by bromination with N-bromosuccinimide followed by dehydrobromination using pyridine. In order to synthesize 4-phenylcoumarins, the reaction of phenols with phenylpropiolic acid ethyl ester was further studied. Resorcinol and phloroglucinol when condensed with phenylpropiolic acid ethyl ester in presence of anhydrous zinc chloride gave XVIIa[9] and XVIIb[10] respectively. Hydroxyquinol triacetate in a similar condensation with phenylpropiolic acid ethylester gave nordalbergin (XVIII), identical in all respects with a natural sample.[11]



XVI



XVIIa: R = H
XVIIb: R = OH



XVIII

EXPERIMENTAL*

Reaction of 5,7-dihydroxy-2,2-dimethylchroman-4-one with ethyl propiolate

A stirred mixture of 5,7-dihydroxy-2,2-dimethylchroman-4-one (4·16 g), ethyl propiolate (2·94 g) and anhyd $ZnCl_2$ (2·72 g) was heated at 100° for 1 hr. It was then cooled, digested with cold 2N HCl and extracted exhaustively with ether. The ether-extract was washed with 5% $NaHCO_3$ aq. H_2O, dried over Na_2SO_4 and the solvent removed. The crude product (3·5 g) on TLC showed it to be a mixture of two very closely moving substances.

The mixture was dissolved in benzene and chromatographed on a column of Si gel (35 g) in benzene. Fractions (50 ml) were collected and the progress of the chromatogram followed by TLC.

TABLE 1

Fractions	Eluent	Weight	R_f (Chf)
1–4	Benzene	–	
5–6	Benzene	110 mg	0·48
7	Benzene	120 mg	0·48, 0·41
8–12	Benzene (Chf 20%)	435 mg	0·48, 0·41
13–18	Benzene (Chf 20%)	280 mg	0·41
19	Chf		
20	MeOH	2 g	Gum

* UV and IR spectra were determined on Beckmann DU and Perkin-Elmer Model 421 spectrophotometers. NMR spectra were taken on a Varian A-60 spectrophotometer in $CDCl_3$ solutions with TMS as internal reference standard. M.ps are uncorrected.

[8] J. C. Bell, W. Bridge and A. Robertson, *J. Chem. Soc.* 1542 (1937).
[9] H. Pechmann and C. Duisberg, *Ber. Dtsch. Chem. Ges.* **16**, 2126 (1883).
[10] S. Kostanecki and G. Weber, *Ber. Dtsch. Chem. Ges.* **26**, 2907 (1893).
[11] V. K. Ahluwalia and T. R. Seshadri, *J. Chem. Soc.* 970 (1957).

Isolation of clausenin

A. Fractions 5–6 were combined and the solvent removed. The residue was crystallized from CH_2Cl_2–hexane (I: 55 mg), m.p. 155°. (Found: C, 64·7; H, 4·7. $C_{14}H_{12}O_5$ requires: C, 64·6; H, 4·7%.) The compound did not show any depression in its m.p. when mixed with a sample of natural clausenin. Its identity was further confirmed by identical TLC behaviour and superimposable IR and NMR spectra.

6,7-*Dihydro*-6,6-*dimethyl*-9-*hydroxy*-8-*oxo*-*pyrano* [2,3-f]*coumarin* (IIa)

B. Fractions 13–18 were combined, the solvent removed and the residue crystallized from CH_2Cl_2–hexane (IIa: 160 mg), m.p. 220°. λ_{max}^{alk} 278, 324 mμ (log ε, 4·49, 4·15). IR (Nujol) 1730, 1650, 1625, 1590, 1400, 1330, 1308, 1282, 1260, 1225, 1185, 1162, 1150, 1118, 1098, 1088, 955, 922, 908, 885, 862, 795, 775, 760, 715, 690 cm^{-1}. NMR peaks 12·1 (S, OH), 7·9 (1H, d, J = 10 c s; C-4 proton of coumarin), 6·37 (1H, S, aromatic proton), 6·15 (1H, d, J = 10 c s; C-3 proton of coumarin), 2·83 (S, 2H,), 1·53 (6H, S, ). (Found: C, 64·8; H, 4·9. $C_{14}H_{12}O_5$ requires: C, 64·6; H, 4·7%.)

C. Fractions 7–12 were combined and the solvent removed. The residue (550 mg), a mixture of clausinin and its angular isomer, was dissolved in MeOH (15 ml) and ether (135 ml) and excess diazomethane added. The reaction mixture was allowed to stand at room temp for 4½ hr. Unreacted diazomethane was decomposed with a few drops of AcOH and the solvent removed. When the crude product was treated with ether containing a few drops of MeOH the gummy portion went in soln leaving behind the semi-crystalline residue. This was isolated by filtration (260 mg). TLC examination showed it to be a mixture of two substances which were separated by chromatography on a column of Si-gel (3 g) in benzene. Fractions (10 ml) were collected and the progress of the chromatogram followed by TLC.

TABLE 2

Fractions	Eluent	Weight	R_f (Chf)
1–4	Benzene	–	
5–10	Benzene	60 mg	0·22
11–20	Benzene	25 mg	0·22, 0·18
21–28	CHf	15 mg	0·22, 0·18
29–40	CHf	150 mg	0·18

Isolation of clausenin monomethyl ether

(i) Fractions 5–10 were combined, the solvent removed and the residue crystallized from CH_2Cl_2–ether (50 mg), m.p. 147–149°. A mixed m.p. with clausenin monomethylether was undepressed and the identity was further confirmed by identical TLC behaviour and superimposable IR spectra.

6,7-*Dihydro*-6,6-*dimethyl*-9-*methoxy*-8-*oxo*-*pyrano* [2,3-f] *coumarin* (IIb)

(ii) Fractions 29–40 were combined, the solvent removed and the residue crystallized from CH_2Cl_2–ether (IIb: 125 mg), m.p. 193–194°. λ_{max}^{alk} 210, 275, 324 mμ (log ε, 4·24, 4·42, 4·15). IR (Nujol) 1730, 1682, 1610, 1598, 1480, 1400, 1328, 1285, 1260, 1230, 1208, 1185, 1155, 1125, 1105, 1095, 985, 960, 910, 890, 865, 832, 822, 812, 785, 768, 720 cm^{-1}. NMR peaks 8·0 and 6·21 (1H, each d, J = 10 c s, C-4 and C-3 protons), 6·41 (1H, S, aromatic proton), 4·0 (3H, S, OCH_3), 2·75 (2H, S,), 1·55 δ (6H, S, ).

(Found: C, 65·8; H, 5·0. $C_{15}H_{14}O_5$ requires: C, 65·7; H, 5·2%.)

Reduction of clauseninmonomethyl ether with $NaBH_4$

Clausenin monomethyl ether (500 mg) dissolved in pyridine (7 ml) and H_2O (3·5 ml) was treated dropwise with a soln of $NaBH_4$ (280 mg) in H_2O (3·5 ml). The reaction mixture was heated at 70° for 1 hr, cooled and acidified with 2N HCl. It was thoroughly extracted with CH_2Cl_2. The CH_2Cl_2 extract was successively washed with dil. HCl, 5% $NaHCO_3$ aq, H_2O and dried over Na_2SO_4. Removal of the solvent gave a gummy residue (400 mg), which showed 3 spots on TLC. The gum was dissolved in benzene and chromatographed on a column of Si-gel. Fractions (5 ml) were collected and the progress of the chromatogram followed by TLC.

TABLE 3

Fractions	Eluent	R_f Chf AcOEt (19:1)
1–30	Benzene	
31–50	Benzene	0·54, 0·41
51–60	Benzene	—
61–70	Benzene + Chf 25%	
71–90	Chf	0·11
91–95	MeOH	Gum

Fractions 71–90 were combined and the solvent removed. The residue crystallized from ether–pentane to give V (115 mg), m.p. 142°, λ_{max}^{alc} 206, 250, 262, 328 mμ (log ε, 4·50, 3·68, 3·79, 4·20). IR (Nujol) 3525, 1740, 1620, 1560, 1400, 1350, 1338, 1315, 1270, 1260, 1248, 1210, 1180, 1145, 1105, 1080, 1045, 945, 905, 895, 880, 842, 825, 718 cm^{-1}. NMR peaks: 7·5, 6·25 (1H each, d, J = 10 c/s, C-4 and C-3 protons of coumarin), 7·61 (1H, S, aromatic proton), 5·1 δ (1H, t, J = 7 c/s), 4·1 (3H, S, OCH_3), 3·2 (1H, OH), 2·1 (2H, d, J = 7 c/s), 1·48, 1·4 (3H each, S, $C(Me)_2$). (Found: C, 65·0; H, 5·8. $C_{15}H_{16}O_5$ requires: C, 65·2; H, 5·8.)

Dehydration of V *to xanthoxyletin*

The secondary alcohol (15 mg) was mixed intimately with fused $KHSO_4$ (50 mg) and heated at 90–100°/0·1 mm in a sublimation tube. The product which sublimed had a m.p. 130°. This substance did not show any depression when mixed with an authentic sample of xanthoxyletin. Its identity with xanthoxyletin was further confirmed by TLC behaviour and superimposable IR (KBr) and NMR spectra.

Alloxanthoxyletin VIII

Compound IIb (420 mg), m.p. 193–194°, dissolved in pyridine (5 ml) and H_2O (2·5 ml) was treated dropwise with a soln of $NaBH_4$ (210 mg) in H_2O (2·5 ml). The reaction mixture was heated at 70° for 1 hr, cooled and acidified with 2N HCl. It was thoroughly extracted with CH_2Cl_2. The CH_2Cl_2 extract was successively washed with dil. HCl, 5% $NaHCO_3$ aq, H_2O and dried over Na_2SO_4. Removal of the solvent gave a gummy residue mixed with a crystalline matter (250 mg). TLC examination indicated this to contain 3 compounds. This mixture was chromatographed on a Si-gel column in Chf. Fractions (5 ml) were collected and the progress of the chromatogram followed by TLC.

Fractions 9–19 were pooled, the solvent removed and the residue obtained crystallized from CH_2Cl_2–ether (30 mg), m.p. 135°. This compound was mixed intimately with fused $KHSO_4$ (250 mg) and sublimed at 2×10^{-3} mm/110°. The product which sublimed had a m.p. 115–116° (Alloxanthoxyletin lit.[6] m.p. 115–116°).

TABLE 4

Fractions	Eluent	Weight	R_f Chf AcOEt (19:1)
1–2	Chf	40 mg	0·70, 0·56
3–5	Chf	65 mg	0·70, 0·56
6–8	Chf	11 mg	0·56, 0·11
9–19	Chf	48 mg	0·11

Dihydroalloxanthoxyletin (X)

A stirred mixture of IX[2] (1·5 g), ethyl propiolate (0·784 g) and anhyd. $ZnCl_2$ (0·91 g) was heated at 100° for 1 hr. It was then cooled, digested with 2N HCl and extracted exhaustively with ether. The ether-extract was washed with 5% $NaHCO_3$ aq., H_2O, dried over Na_2SO_4 and solvent removed. A gummy residue mixed with crystalline matter was obtained (1·3 g). This was dissolved in MeOH (25 ml) and ether (75 ml), and treated with excess diazomethane. The reaction mixture was allowed to stand at room temp for 6 hr. Unreacted diazomethane was decomposed with a few drops of AcOH, and the solvent removed. The residue obtained was dissolved in benzene and chromatographed on a column of Si-gel (15 g) in benzene. Fractions (15 ml) were collected and the development of the chromatogram followed by TLC.

TABLE 5

Fractions	Eluent	Weight	R_f Benzene–Chf (2:3)
1–3	Benzene	--	
4–10	Benzene	50 mg	0·73, 0·64
11–18	CHf	160 mg	0·73, 0·64
19–27	CHf	20 mg	Gum
28–30	MeOH	800 mg	Gum

Fractions 4–18 were combined and the solvent removed. The resulting semi-crystalline residue crystallized from hexane containing a few drops of ether.

(i) The first crop separated as clusters of needles (X, 42 mg). TLC on Si-gel: R_f 0·64 (Benzene : Chf, 2:3), m.p. 153–155° (Dihydroalloxanthoxyletin lit.[6] m.p. 153°). λ_{max}^{alc} 210, 248, 256 and 326 mμ (log ε 4·5, 3·9, 3·9 and 4·2). IR (KBr) 1720, 1610, 1568, 1488, 1442, 1428, 1392, 1365, 1330, 1312, 1270, 1252, 1240, 1200, 1158, 1120, 1105, 1020, 988, 930, 915, 900, 880, 830, 815, 792, 758, 740 cm^{-1}. NMR peaks at 8·0, 6·2 (1H each, d, J = 10 c/s, C-4 and C-3 protons), 6·41 (1H, S, aromatic proton), 3·9 (3H, S, $-OCH_3$), 2·68, 1·8 (2H each, triplet J = 6 c/s; $-CH_2-CH_2-$), 1·38 δ (6H, S, $-C(Me)_2$). (Found: C, 69·4; H, 6·3. $C_{15}H_{16}O_4$ requires: C, 69·2; H, 6·2%.)

8,9-*Dihydro*-8,8-*dimethyl*-5-*methoxy*-*pyrano*-[2,3-h]*coumarin*

(ii) The mother liquor after separation of dihydroalloxanthoxyletin, deposited a crop of heavy prisms (XI, 46 mg), m.p. 162°. TLC on Si-gel: R_f 0·73 (Benzene : Chf, 2:3). λ_{max}^{alc} 206, 254, 264 and 336 mμ log ε 4·45, 3·96, 3·99 and 4·22). IR (KBr) 1705, 1620, 1600, 1490, 1465, 1432, 1382, 1370, 1360, 1330, 1308, 1270, 1250, 1230, 1200, 1185, 1155, 1135, 1110, 1085, 1032, 1020, 990, 960, 932, 910, 895, 880, 830, 820, 810, 770,

755, 730, 690, 660, 650, 625, 610 cm^{-1}. NMR peaks at 8·0, 6·15 (1H each, d, J = 10 c/s, C-4 and C-3 protons of coumarin), 6·25 (1H, S, aromatic proton), 3·9 (3H, S, $-OCH_3$), 2·82, 1·82 (2H each, triplet, J = 7 c/s, $-CH_2-CH_2-$), 1·35 δ (6H, S, ). (Found: C, 69·4; H, 6·2. $C_{15}H_{16}O_4$ requires: C, 69·2; H, 6·2%.)

6,7-Dihydro-6,6-dimethyl-8-oxo-pyrano[2,3-f]coumarin (XV)

A stirred mixture of ethyl propiolate (4·9 g), 2,2-dimethyl-7-hydroxy chromanone (5·5 g) and anhyd $ZnCl_2$ (4 g) was heated at 100° for 1 hr. The reaction mixture was cooled, triturated with 2N HCl and extracted with ether. The ether extract was washed with water, dried over Na_2SO_4 and distilled to yield an oil. It was chromatographed on Si-gel and on elution with benzene two crystalline compounds were obtained:

(a) trimesic acid triethyl ester $C_{15}H_{18}O_6$ (XIV), m.p. 135°; NMR spectrum showed signals at 1·4 (9H, triplet J = 10 c/s), 4·5 (6H, quartet J = 8 c/s, $-CH_2-$), 8·9 δ (3H, S, aromatic protons).

(b) Compound XV crystallized from pentane, m.p. 217–218°, ν_{max} 1600, 1620, 1730, 1740 cm^{-1} (coumarin), 1690 cm^{-1} (aromatic ketone). λ_{max} 212, 268 log ε, 4·08, 4·4. (Found: C, 68·6; H, 5·0. $C_{14}H_{12}O_4$ requires: C, 68·8; H, 5·0%.) NMR spectrum shows signals 1·7 (6H, S, *gem*-dimethyl), 2·8 (2H, S), 6·42 (1H, d, J = 10 c/s), 6·96 (1H, d, J = 10 c/s), 8·06 (1H, d, J = 10 c/s) and 8·12 δ (1H, d, J = 10 c/s).

Xanthyletin (XII)*

A soln of dihydroxanthyletin in CCl_4 (6 ml) was refluxed with N-bromosuccinimide (250 mg) for 6 hr. The reaction mixture was cooled, filtered and distilled. The crude bromo compound was dehydrobrominated by heating on a water bath with pyridine (2 ml) for 2 hr. Working up in the usual way yielded an oil which sublimed at 100°/10^{-4} mm as colourless solid. After crystallization from pentane it melted at 120° alone or when mixed with an authentic sample of xanthyletin.

5,7-Dihydroxy-4-phenyl coumarin (XVIIb)

A mixture of phloroglucinol (2·5 g), phenyl propiolic acid ethyl ester (5 g) and anhyd $ZnCl_2$ (3 g) was heated at 100° for 2 hr. The reaction mixture was cooled, triturated with 2N HCl and extracted with ether. The ether extract was washed with water, dried and distilled to yield an oil which on standing with a small amount of AcOEt yielded 5,7-dihydroxy-4-phenylcoumarin (0·5 g). It was recrystallized from AcOEt, m.p. 235°. (Found: C, 70·5; H, 3·7. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 4·0%.)

7-Hydroxy-4-phenylcoumarin (XVIIa)

A mixture of resorcinol (2·1 g), phenyl propiolic acid ethyl ester (5 g) and anhyd $ZnCl_2$ (3 g) was heated at 100° for 2 hr. The reaction mixture was worked up as above yielding 7-hydroxy-4-phenylcoumarin (0·4 g), m.p. 242–244°. (Found: C, 75·3; H, 4·01. Calc. for $C_{15}H_{10}O_3$: C, 75·62; H, 4·23%.)

6,7-Dihydroxy-4-phenylcoumarin (*Nordalbergin*, XVIII)

A soln of hydroxyhydroquinone triacetate (5·5 g) and phenylpropiolic acid ethyl ester (6 g) in abs EtOH (32 ml) was heated under reflux for 14 hr with conc H_2SO_4 (6 ml). The solvent was removed, ice was added and extracted with ether. The ether extract was washed with water, dried over Na_2SO_4 and distilled to yield an oil which solidified on standing with AcOEt. It was recrystallized from AcOEt yielding 1·5 g of nordalbergin, m.p. 274–276°. (Found: C, 70·6; H, 3·8. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 4·0%.) Mixed m.p. with an authentic sample was not depressed.

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