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CONSTITUENTS OF *SURIANA MARITIMA*: A TRITERPENE DIOL OF NOVEL STRUCTURE AND A NEW FLAVONOL GLYCOSIDE

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Abstract-Suriana *maritima* L., often classified in Simaroubaceae, but regarded also as the monotypic member of Surianaceae, is devoid of the terpenoid lactones that characterize Simaroubaceae. It contains a novel triterpenoid diol, surianol, the structure of which is described. In addition to this, β-sitosterol, rutin. and rhamnetin-3-rutinoside, the latter a new flavonol glycoside, were also found as constituents of the plant.

INTRODUCTION

Suriana maritima L., a pantropical shrub or small tree common to coral coasts of Pacific–Indian Ocean islands and to the coast of Florida, has had an uncertain taxonomic history. Although the most recent classifications placed it in a monotypic family, Surianaceae, allied to Stylobasiae and Simaroubaceae,[1,2] Nooteboom,[3] after a consideration of earlier discussions, accepts the classification in Simaroubaceae.

In view of the large body of evidence that simaroubaceous genera are uniformly characterized by their content of bitter lactones allied to such now well known compounds as quassin, chaparrin, glaucarubol and many others,[4] it appeared likely that an investigation of its chemistry might provide information to support one or the other of the conflicting taxonomic opinions.

RESULTS AND DISCUSSION

Suriana maritima, collected in Florida,† was dried and powdered and extracted with methanol.[5] Concentration of the initial extract and dilution with water resulted in the deposition of a generous quantity (0·55% of the dry wt. of plant) of a yellow crystalline material, readily recognized as flavonoid in character. Several recrystallizations of this material led to its separation into two pure (by TLC) components. One of these was identified as rutin (I), the other as 7-*O*-methylrutin (rhamnetin 3-rutinoside) (II). Acid hydrolysis of I and II led to the formation, respectively, of quercetin and rhamnetin, characterized as the acetates. Both I and II gave rhamnose and glucose upon hydrolysis, and methylation

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† We are grateful to Dr. William Gillis for his generosity in collecting the plant material used in this work.

[1] A. CRONQUIST, *The Evolution and Classification of Flowering Plants,* Houghton-Mifflin, Boston (1968).

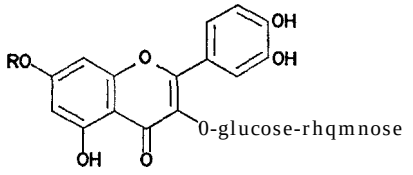
[2] J. C. WILLIS, *A Dictionary of the Flowering Plants and Ferns* (7th edition revised K. AIRY-SHAW), Cambridge University Press, Cambridge (1966).

[3] H. P. NOOTEBOOM, *Flora Malesiana, Ser. Z 6, 193 (1962).*

[4] For examples, see J. POLONSKY, Les Principes Amers des Simarubacées, *Planta Med., Suppl. 107 (1966).*

[5] Neither the ground plant material nor the extract was bitter, a fact which has been noted by others and used in arguments to support early classifications. It is to be noted, however, that *Holacantha emoryi* (Simaroubaceae), recently shown to contain glaucarubol (W. STÖCKLIN, L. B. DE SILVA and T. A. GEISSMAN, *Phytochem. 8, 1565* (1969)), lacks the bitterness common to other simaroubaceous species.

and hydrolysis of I and II gave the same compound, 3′,4′,5,7-tetra-*O*-methylquercetin. The trimethylsilyl derivative of I gave an NMR spectrum identical with that described for rutin.[6] The trimethylsilyl derivative of II gave an NMR spectrum essentially identical in all details with that of I (and rutin) except for the appearance of a three-proton singlet at δ 3·90 for the 7-methoxyl group. These data establish the identity of the new flavonol as rhamnetin 3-rutinoside (II).



I, R=H
II, R = CH_3

Concentration of the residual methanolic solution and extraction with light petroleum afforded an extract which contained the bulk of the total extractives; it was not bitter. Repartition of the petroleum-extractives between pentane and methanol-water (1: 1) gave a pentane solution which was closely examined.

Chromatography of the pentane solution over silica gel yielded, first, β-sitosterol,* and in later fractions, surianol, (III), m.p. 173–174·5°, $C_{29}H_{48}O_2$ (high resolution mass spectrum; molecular ion at *m/e* 428). Surianol readily formed a diacetate (IV), the analysis and mass spectrum of which agreed with the constitution $C_{33}H_{52}O_4$. That surianol was a triterpenoid was indicated by the mass and NMR spectra. The latter showed two tertiary methyl groups and the geminal dimethyl grouping of an isopropyl group, which appeared as a 6-proton doublet (J = 6·5 Hz) at δ 1·03 ppm. Two hydroxyl protons (lost after exchange with D_2O) were seen at δ 2·80, the two non-equivalent carbinol protons of the secondary alcohol groupings appearing as a triplet (J = 9 Hz) at δ 3·09 and a broad multiplet at δ 3.43. After the addition of D_2O the latter signal had the appearance of a doublet of triplets at S 3·43 and 3·46 with J = 9, 9 and 4 Hz. Two one-proton doublets at δ 0·47 and 0·13 ppm (J = 4 Hz) were indicative of a cyclopropyl grouping bearing two geminal protons only.[7] Two one-proton (broadened) singlets at δ 4·66 and 4·71 indicated the presence of a terminal methylene group.

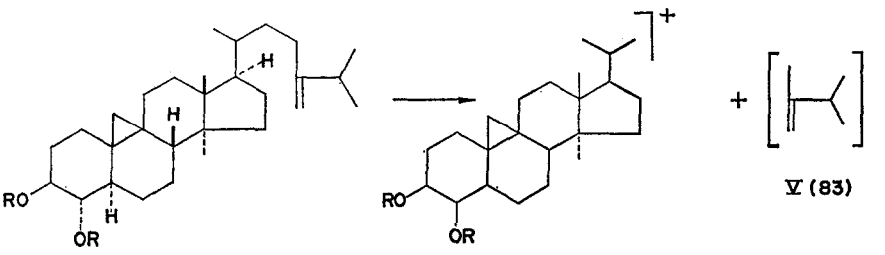
The mass spectrum showed a fragment ion at M^+-125 which can be accounted for by loss of the side-chain, which can be formulated as the 24-methylenecholestane side-chain. In accord with this, the dihydrodiacetate showed a fragment ion at M^+-127. The placing of the side-chain methylene group at C-24125 is supported by the appearance in the mass spectra of III and its derivatives of a fragment M+-83, ascribed to the ion resulting from the loss of the

* The constants observed for this compound were in satisfactory agreement with those of β-sitosterol, but the mass spectrum disclosed a small peak at *m/e* 416 (β-sitosterol = 414), indicating the presence of a small amount of a dihydro compound, probably stigmastanol.

[6] T. J. MABRY, J. KAGAN and H. RÖSLER, *NMR Analysis of Flavonoids*, Univ. of Texas Publ., No. 6418 (15 September 1964).

[7] G. BERTI, F. BOTTARI, B. MACCHIA, A. MARSILI, G. OURISSON and H. PIOTROWSKA, *Bull. Soc. Chim. France 2359 (1964).*

allylic radical (V) from the side chain by cleavage at the C-22/23 bond. In agreement with this view, the dihydro compound showed no corresponding ion.



III, R = H
IV, R = $COCH_3$

m/e 345

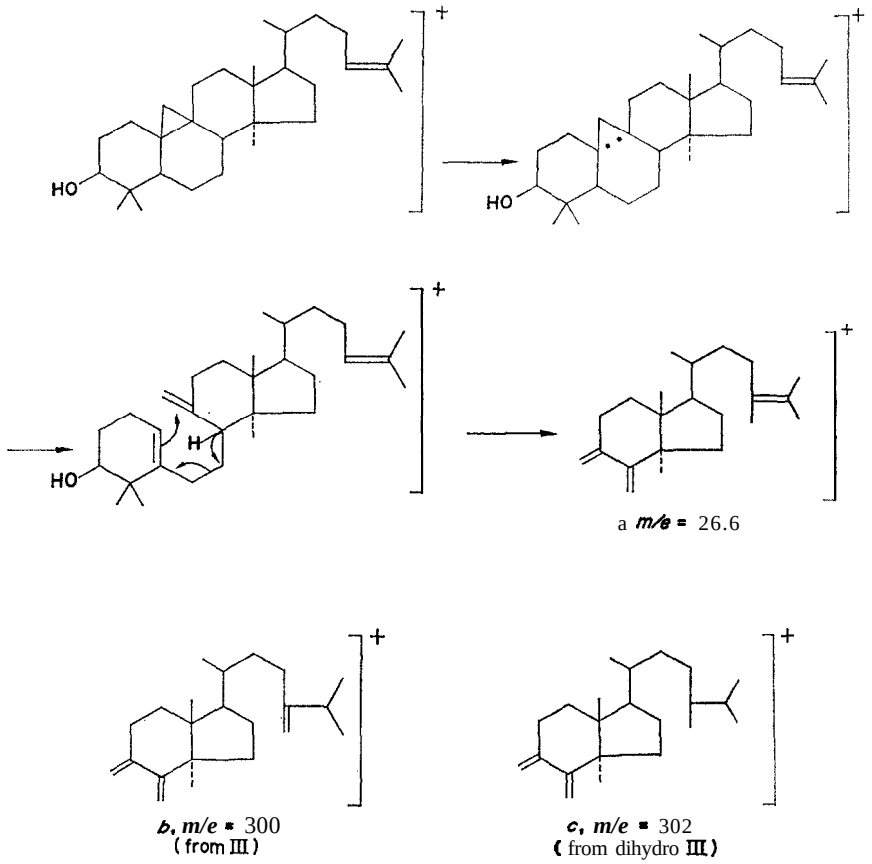
The placing of the cyclopropane ring at the 9,10-position is, of course, favored on biogenetic grounds, for numerous triterpenes containing this structure are known. Support for this assignment is found in the fragmentation patterns of I and its derivatives. Surianol, and derivatives bearing the methylene group at C-24, show fragment ions at m/e 300 and *m/e* 175 (loss of side chain from m/e 300). 9,10-Cyclotriterpenes (e.g. VI) characteristically show a fragment a (Scheme I) in their mass spectra.[8] The formation of fragments ***b*** (from III) and c (from the dihydro derivatives) are consistent with this mode of fragmentation. Moreover, the formation of ***b*** and c make it necessary to conclude that the two hydroxyl groups are found in the A ring, and that no carbon atoms (e.g. 4-CH_3) are attached to ring A. Thus, ion fragment ***b*** contains all of the methyl groups present in the parent compound.

In summary, all of the above evidence leads to the proposal of structure III for surianol. The placing of the methyl groups at C-13 and C-14 is on biogenetic grounds, but it will be seen that no other reasonable accommodation can be made for other skeletal dispositions of the methyl groups in the fragment ions ***b*** and c.

Additional evidence for the structure of ring A was found in the following way. Surianol formed an acetonide, showing the vicinal disposition of the hydroxyl groups. The i.r. spectrum of III in dilute carbon tetrachloride solution showed free and intramolecularly bonded hydroxyl stretching vibrations at 3610 and 3570 cm-', values typical of a-glycols. Oxidation of III with chromic acid (e.g. Jones' reagent) gave varying results, depending upon the conditions used. One product was a dicarboxylic acid, formulated as VII.

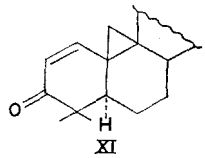
Oxidation to the dicarboxylic acid appears to proceed through the two intermediate a-ketols as shown by TLC, using as a reference standard one of the a-ketols isolated in an alternative oxidation in which chromic acid in acetic acid was used. The dimethyl ester (VIII) of the acid showed two carbomethoxy groups in its NMR spectrum, and a mass spectral molecular ion at *m/e* 486. A high resolution mass determination agreed closely with the expected composition $C_{31}H_{50}O_4$. In addition to the dicarboxylic acid, oxidation yielded an a-ketol which was easily oxidized with bismuth trioxide in acetic acid. The mixture of products, which could not be separated nor individually characterized, showed mass spectral molecular ions at *m/e* 424 (for a diosphenol) and *m/e* 422, the latter being assumed to be the 1-ene-3,4-dione (X) resulting from further oxidation of the diketone (IX) (diosphenol). Support for this interpretation is found in the u.v. spectrum of the mixture, which showed

[8] H. E. AUDIER, R. BEUGELMANS and B. C. DAS, *Tetrahedron Letters 4341 (1966).*



SCHEME 1.

λ_{max} at 310 nm, shifted to 352 nm after addition of alkali, a shift characteristic of diosphenol.[9,*] Although the usual range of absorption for the diosphenol chromophore is 270-280 nm, the absorption of a chromophore conjugated with a cyclopropane ring often undergoes *a* bathochromic shift which is normally 10–12 nm[9] but which has been reported to be as high as 40 nm in the structure XI.[9]



XI

λ_{max} 269 nm

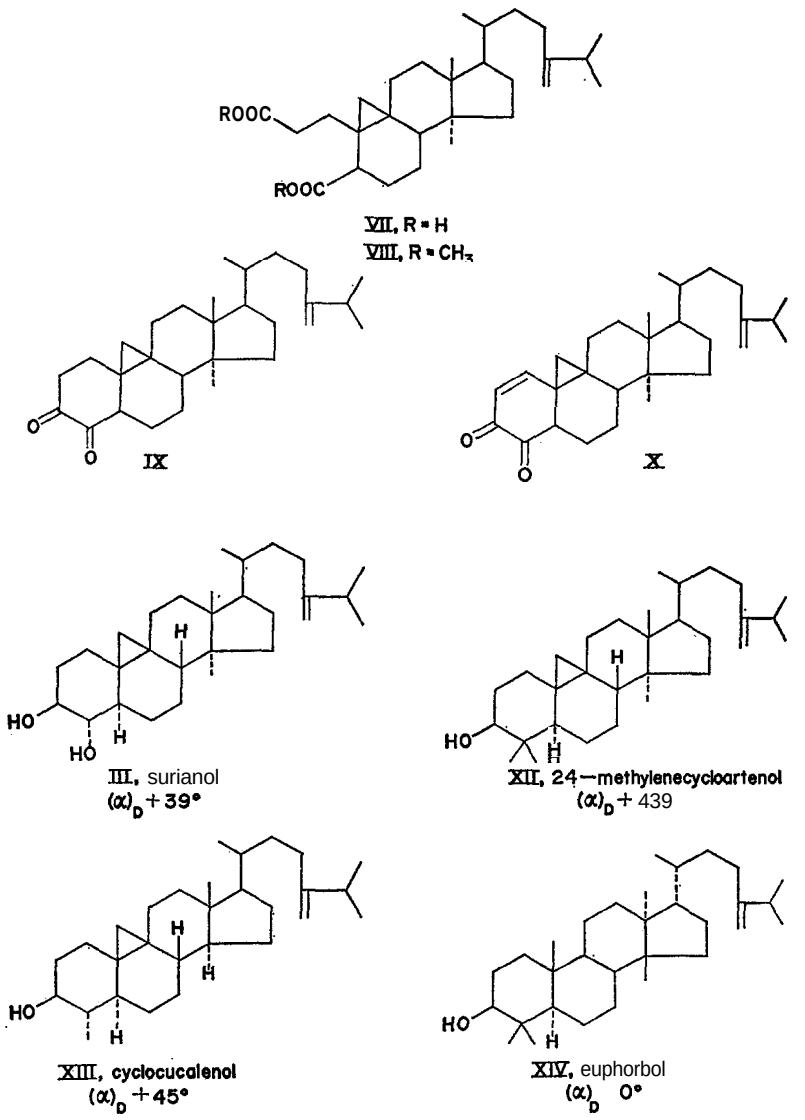
The formation of a dehydrodiosphenol is regarded as supporting evidence for an A-ring diol system in a 9,10-cyclocarbocyclic skeleton in which the tertiary methyl groups are found at the C/D ring junction. Oxidation of diols in which the hydroxyl groups were at 6,7-,

* When a TLC plate of the mixture was sprayed with ferric chloride solution a dark spot appeared at the position to which the compound(s) migrated.

[9] I. A. SCOTT, *The Interpretation of Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford (1964).

11,12-, 15,16- or 16,17- would not proceed past the diketone stage (short of more extensive degradation). It is compelling on biogenetic grounds to place one of the hydroxyl groups at C-3β, thus leaving a choice between a 2,3- and a 3,4-diol. The carbinol proton signals in the NMR spectrum of III are consistent only with the 3,4-diol, where the 3,4,5-hydrogen atoms are *trans*-diaxially disposed, thus accounting for the triplet with 9 Hz coupling observed for the C-4 proton, and the doublet (4 Hz) of triplets (J = 9, 9 Hz) for the C-3 proton.

Although certain other stereochemical features of surianol are not established with certainty, it seems likely that the stereochemistry shown in III is correct. Surianol has



SCHEME II.

$[\alpha]_D$ + 39°, comparable to other compounds of this class (cf. XII and XIII), but quite different from those recorded for compounds of the euphol (XIV) or tirucallol series.

Although the occurrence in nature of a 4-bisnormethyl triterpene is not new (e.g. macdougallin),[10] the 3,4-diol is unique in the series. It is noteworthy, in respect to the taxonomic question to which this study was originally addressed, that surianol belongs to a stereochemical series different from that which includes the triterpenes (euphol or tirucallol) from which the simaroubaceous lactones are presumably derived.

EXPERIMENTAL

M.ps were determined on a Büchi melting point apparatus and are corrected. I.r. spectra were taken as nujol mulls unless otherwise specified; NMR spectra were recorded in $CDCl_3$ solution unless otherwise specified and peak positions are given in δ values with tetramethylsilane as internal standard; mass spectra were obtained on AEI-MS-9 and CEC-MS-21-491 spectrometers, with direct inlet, at 70 eV ionization potential, and significant ions of higher m/e values as well as ions with relative abundance of 40 % or more of the base peak are quoted with their relative abundance in parenthesis. TLC was run on precoated Merck F_{254} plates (5 × 10, or 5 × 20 cm when the adsorbate was particularly complex), visualization being satisfactory after spraying with conc. H_2SO_4 and heating in an oven at 120" for a few min; column chromatograms used Baker silica gel 60-200 mesh (30 g/l g of adsorbate) packed in hexane or benzene and were eluted with the appropriate solvent (usually increasing portions of Et_2O, then increasing portions of acetone in Et_2O), their progress always being monitored by TLC analysis of the fractions collected. Analytical samples were dried at 80°/0·1 mm or 1 10°/0·1 mm for 16 hr immediately prior to analysis.

Extraction of Suriana maritima. 1 kg of dried powdered plants was processed as recorded in the summarized form of Scheme III. Each extract was separately examined on TLC and since the $CHCl_3$ and $CHCl_3$–methanol extracts appeared the same they were combined.

7-O-*Methylrutin (II)*, was obtained as yellow needles after recrystallization of the crude yellow solid several times from methanol (filtered hot); it was less soluble in methanol than rutin; TLC R_f 0·34 (rutin 0·25) after development with $CHCl_3$–MeOH–H_2O (55:35: 10); red color in mg/conc. HCl; δ (CCl_4, trimethylsilyl derivative) 7.45 (H-6' doublet of doublets, J = 2, 8 Hz), 7·40 (H-2', d, J = 2 Hz), 6·87 (H-5', d, J = 8 Hz), 6.48 (H-8, d, J = 2·5 Hz), 6.23 (H-6, d, J = 2·5 Hz), 5.82 (glucose H-l, broadened d, J = 6 Hz), 427 (rhamnose H-l, s), 3·82 (—OCH_3), and 3·8–3·1 (10 carbohydrates protons); λ_{max} (log ε) 257 (4·45), 265 (shoulder) (4·30), 297 (3.92) and 361 (4.27) nm; λ_{min} 238 (4·10), 282 (3.87) and 307 (3.91) nm.

Hydrolysis of this compound (250 mg) proceeded by refluxing for 2 hr in methanol (10 ml) containing 10 % aq. H_2SO_4 (10 ml). Cooling and filtration afforded a yellow crystalline solid which was dried, dissolved in pyridine (2 ml) and acetylated with acetic anhydride (1·5 ml) by standing at room temperature for 24 hr. The reaction was poured into iced 2N HCl and the product extracted with $CHCl_3$; the combined $CHCl_3$ extract was washed with portions of 2N HCl, then saturated $KHCO_3$ solution, and after drying and filtration was evaporated, affording colorless needles (1.50 mg) after recrystallization of the residue from ethanol, m.p. 190–192°, with spectral properties (I.r., NMR and mass spectra) consistent for rhamnetin tetraacetate (lit." m.p. 192-193'). ***Anal.*** Found: C, 59.58; H, 444; calc. for $C_{24}H_{20}O_{11}$: ***C, 59.50;*** H, 4·16%. Hydrolysis of this compound (100 mg) by refluxing it for 3 hr in methanol (7.5 ml) containing 10 % aq. H_2SO_4 (5 ml) gave a yellow crystalline product which was filtered from the cooled reaction mixture; 58 mg, m.p. 295298" (dec.) (lit." for rhamnetin 294-296"). The aqueous solution remaining after hydrolysis of the glycoside was neutralized ($Ba(OH)^2$ solution), filtered, then studied on thin layer chromatograms of silica gel G (Merck) whereby two components were observed, these corresponding in color and in R_f* to glucose and rhamnose when co-chromatographed with each of these and compared with glucose-rhamnose mixtures.

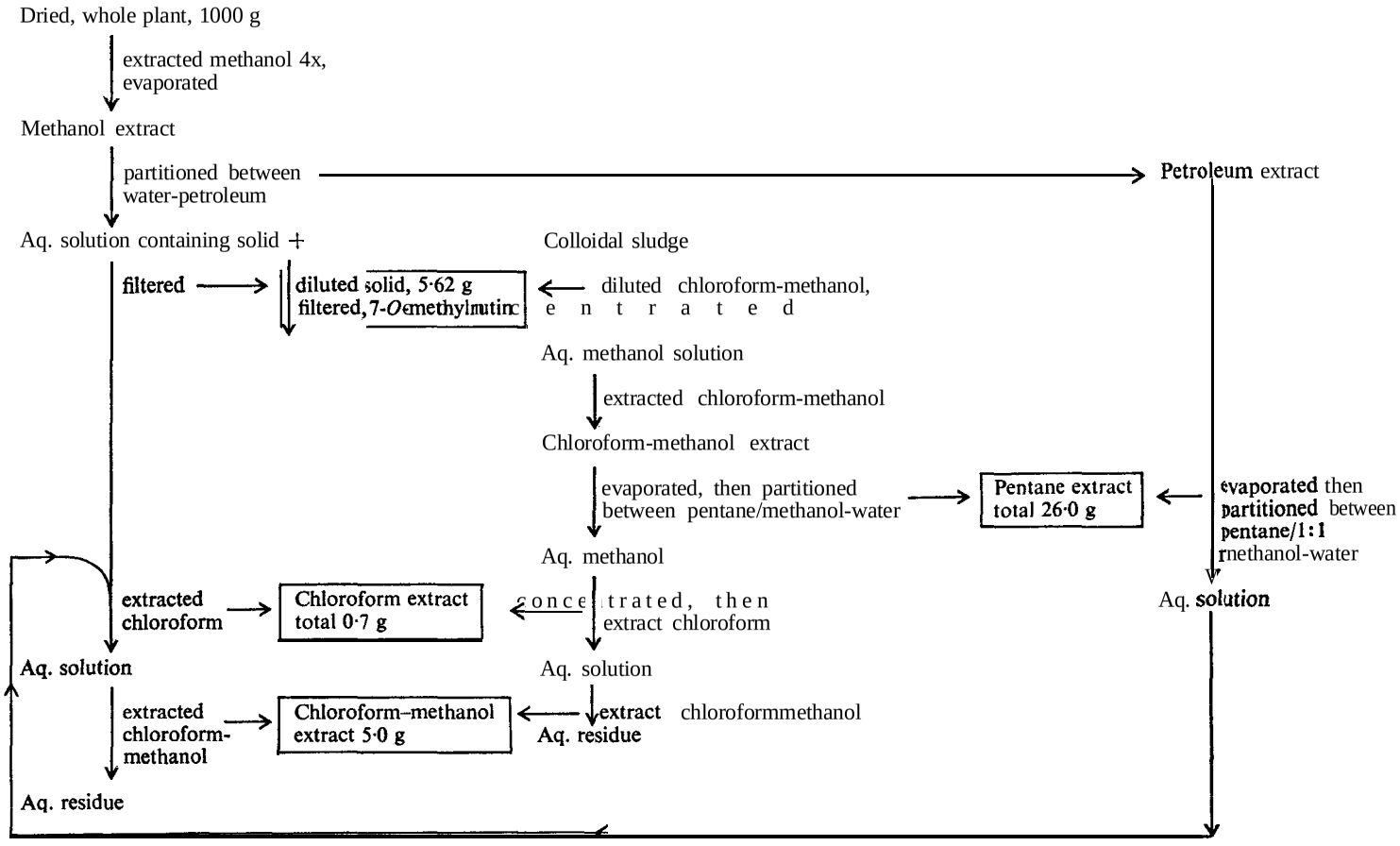
Methylation of II (100 mg) was accomplished by stirring it with anhydrous K_2CO_3 (150 mg) in refluxing acetone (20 ml) containing an excess of Me_2SO_4 (0·15 ml) for 16 hr. The reaction mixture was then evaporated and refluxed for 1 hr with 5 % aq. H_2SO_4 (10 ml). A cream-colored solid was filtered from the cooled solution, dried, then twice recrystallized from ethanol, affording yellow needles (39 mg), m.p. and mixed m.p. with authentic 5,7,3′,4′-tetra-*O*-methylquercetin 201–202°, i.r. spectrum identical with that of authentic material prepared in the same way from rutin.

Rutin (I) was obtained from the mother-liquor remaining after the initial recrystallization of the crude yellow solid. Several successive concentrations of, and recrystallization from, this mother-liquor, led to a

* The chromatograms were developed with n-propyl alcohol–ethyl acetate-water (70–20–10), sprayed with an anisaldehyde spray and heated to show green and blue-black spots, on a pink background, for rhamnose and glucose which had R_f values of 0·58 and0.48, respectively, when chromatographed as a mixture. See E. STAHL, ***Thin-layer Chromatography,*** Springer Verlag, Berlin (1965).

[10] C. DJERASSI, J. C. KNIGHT and D. I. WILKINSON, ***J.*** Am. ***Chem. Soc. 85, 835*** (1963).

[11] T. A. GEISSMAN, The ***Chemistry of Flaconoid Compounds,*** Pergamon Press, Oxford (1962).



SCHEME III. FLOW-DIAGRAM FOR *Suriana maritima* EXTRACTION.

methanol solution which on TLC showed only traces of the higher R_f component (7-*O*-methylrutin) and a major component with TLC R_f identical with that of rutin. Evaporation afforded a yellow crystalline solid m.p. 185–190° (lit.[11] for rutin 190–192°) which after trimethylsilylation had an NMR spectrum identical with that of trimethylsilylated rutin.[6] Hydrolysis yielded an aglycone which formed a pentaacetate, colorless needles, m.p. 201·5–203° (lit.[11] for quercetin pentaacetate 200°) and sugars corresponding in R_f and color (after spraying, as described above) on TLC to rhamnose and glucose. Acid hydrolysis of the acetate afforded a yellow crystalline solid m.p. 313–316° (dec.) (lit.[11] for quercetin 316–318°). Methylation followed by acid hydrolysis gave 5,7,3′,4′-tetra-*O*-methylquercetin.

β-Sitosterol (0·02% of the plant) crystallized out of fractions eluted with Et_2O–hexane (4:6, 1:1) from a column chromatogram (450 g silica gel) of the pentane extract (26 g). Several recrystallizations (ethanol) gave colorless plates, m.p. 139–140°; $[\alpha]_D^{26}$ −33·5° (c = 2·1 in $CHCl_3$) (lit.[12] m.p. 140°; $[\alpha]_D^{26}$ −37° (c = ? in $CHCl_3$); *Anal.* Found: C, 83·90; H, 11·91; calc. for $C_{29}H_{50}O$: C, 83·99; H, 12·15%; δ 5·37 (one vinylic proton multiplet).

The monoacetate, recrystallized from ethanol, had m.p. 123–125°; $[\alpha]_D^{26}$ −36·5° (c = 2·1 in $CHCl_3$) (lit.[12] m.p. 127–128°, $[\alpha]_D^{25}$ −41° (c = 2·1 in chloroform); *Anal.* Found: C, 81·59; H, 11·26; calc. for $C_{31}H_{52}O_2$: C, 81·52; H, 11·48%.

The mass spectrum of the parent sterol showed molecular ions at *m/e* 414 and 416, indicating the presence of a dihydro compound, most likely dihydrositosterol (stigmastanol); the proportion of this dihydro compound is probably insignificant (if it is indeed stigmastanol) when the above physical constants are compared with those of stigmastanol,[12] calc. for stigmastanol, $C_{29}H_{52}O$: C, 83·58; H, 12·58%; $[\alpha]_D^{20}$ +25° (c = 1·1 in $CHCl_3$); and for stigmastanol acetate, calc. for $C_{31}H_{54}O_2$: C, 81·16; H, 11·87%; $[\alpha]_D^{20}$ +14° (C = 1·8 in chloroform).

Compound III (*Surianol*) (0·01% of the plant) crystallized out of acetone solutions of fractions eluted with $CHCl_3$–Et_2O (3:7) from the column chromatogram of the pentane extract. Recrystallization from acetone gave colorless crystals, m.p. 173–174·5°; ν_{max}^{nujol} 3460, 3390, 3210, 3050, 3025, 1630, 1090, 1070, 1060 and 885 cm^{-1}; $\nu_{max}^{CCl_4}$ (0·005 M) 3610, 3570, 3060 and 3020 cm^{-1}; δ 0·13 (1 H, d, J = 4 Hz), 0·47 (1 H, d, J = 4 Hz) 0·90, 0·96 (3 H, s), 1·03 (6 H, d, J = 6·5 Hz), 2·80 (2 H, m, lost after addition of D_2O), 3·09 (1 H, t, J = 9 Hz), 3·43 (1 H, m), 4·66 and 4·71 (2 H of >C=CH_2); δ (C_6D_6) 0·07 (1 H, d, J = 4 Hz), 0·51 (1 H, d, J = 4 Hz), 0·94 (3 H, s), 1·01 (3 H, s), 1·08 (6 H, d, J = 6·5 Hz), 3·25 (1 H, t, J = 9 Hz), 3·45–4·05 (3 H, overlapping multiplets) and 4·86 (2 H, broadened s); *m/e* 428·3668 (M^+), calc. for $C_{29}H_{48}O_2$: 428·3654; *m/e* 428 (M^+) (17), 413 (M^+-15) (10), 410 (M^+-18) (2), 395 (M^+-18-15) (4), 385 (M^+-43) (6), 345 (M^+-83) (6), 330 (M^+-83-15) (8), 303 (M^+-125) (14), 300 (5), 175 (300-125) (18), 121 (43), 109 (46), 107 (57), 95 (84), 93 (49), 81 (62), 69 (78), 67 (43), 55 (100), 44 (57), 43 (43) and 41 (70).

Acetylation of compound III (30 mg) in pyridine (1 ml) containing Ac_2O (0·5 ml) yielded, after recrystallization of the crude product (ethanol), colorless needles (26 mg) m.p. 132–134°; ν_{max} 1740, 1635, 1245, 1045 and 885 cm^{-1}; δ 0·48 (1 H, d, J = 4 Hz), 0·80 (3 H, s), 0·85 (3 H, s), 0·92 (6 H, d, J = 6·5 Hz), 1·89 (3 H, s), 1·90 (3 H, s), 4·54 and 4·59 (2 H, >C=CH_2) and 4·60–4·80 (2 H, overlapping multiplets; containing 1 H triplet centered at δ 4·65?); δ (C_6D_6) −0·12 (1 H, d, J = 4 Hz), 0·34 (1 H, d, J = 4 Hz), 0·84 (3 H, s), 0·93 (3 H, s), 1·07 (6 H, d, J = 6·5 Hz), 1·76 (3 H, s). 1·81 (3 H, s), 4·86 (2 H of >C=CH_2) and 4·90–5·20 (2 H of overlapping multiplets-contains 1 H t centered at δ 5·00?); *Anal.* Found: C, 77·35; H, 10·26; calc. for $C_{33}H_{52}O_4$: C, 77·29; H, 10·22%; *m/e* 512 (M^+) (10·5), 452 (M^+-60) (11·5), 392 (M^+-120) (52·5), 387 (M^+-125) (6), 327 (M^+-60-125) (5), 300 (7), 267 (M^+-120-125), (35), 175 (300-125) (17), 173 (51·5), 147 (45), 145 (45), 133 (60), 131 (52·5), 95 (50), 93 (75), 91 (75), 83 (69), 81 (45), 79 (55), 69 (50), 67 (75), 57 (65), 55 (75), 43 (100) and 41 (85). Hydrogenation of the diacetate (18 mg) in ethanol in H_2 over Pt catalyst at room temp. and small positive pressure for 1 hr led to a colorless residue after filtration and evaporation of the ethanol, which was recrystallized from ethanol thus affording colorless needles of dihydrosurianol diacetate, 8 mg, m.p. 147·5–148·5; ν_{max} 1735, 1250 and 1045 cm^{-1}; *m/e* 514 (M^+) (36), 454 (M^+-60) (33), 394 (M^+-120) (73), 387 (M^+-127) (23), 327 (M^+-60-127) (28), 302 (11), 267 (M^+-120-127) (63), 175 (302-127) (19), 95 (69), 81 (50), 69 (48), 57 (50), 43 (100) and 41 (67).

Hydrogenation of compound III (55 mg) in ethanol in H_2 over Pt catalyst at room temp. and small positive pressure for 1 hr led to the isolation of colorless needles of dihydrosurianol following filtration and recrystallization (ethanol) of the reaction product; 25 mg, m.p. 187–190° (softening at 183–185°); $\nu_{max}^{CCl_4}$ (0·005 M) 3605, 3565 and 3020 (cyclopropane CH_2) cm^{-1}; *m/e* 430 (M^+) (31), 303 (M^+-127) (37), 302 (10), 175 (302-127) (13), 95 (49), 69 (43), 57 (43), 55 (54), 43 (100) and 41 (63).

Formation of an acetonide of compound III (10 mg) in acetone (5 ml) containing *p*-toluenesulphonic acid (1 mg) proceeded slowly and incompletely (TLC); thus, after standing for 1 week (molecular sieves added after one day) the solution was evaporated and the higher R_f (TLC) component was isolated on a column chromatogram packed in and eluted with benzene, as a colorless oil, TLC homogeneous. Crystallization occurred in a slowly evaporated (at room temp.) ethanol solution. $\nu_{max}^{CCl_4}$ (0·0005 M) 3050 and 3020 cm^{-1}; *m/e* 468 (M^+) (6), 410 (M^+-58) (2), 343 (M^+-125) (2), 167 (47·5), 149 (100), 71 (44), 57 (71), 55 (47·5), 43 (79)

[12] ANON., *The Merck Index* (7th edition), Merck & Co., New York (1960).

and 41 (70); δ 0·90, 0·93, 1·01 (d, J = 6·5 Hz), 1·24, 1·30, 2·94 (t, J = 9 Hz), 3·20 (with the appearance of a doublet of multiplets with J = 9 Hz), 4·56 and 4.62.

Oxidation of Surianol

(i) With chromium trioxide. Surianol (III) *(50* mg, 0.117 mM), in a solution of hot acetic acid (5 ml), was heated on a steambath for 1 hr with a 10% (v/v) solution (0·17 ml, 9·5% excess) of CrO_3 in 10% (v/v) aq. acetic acid, and the reaction mixture was then evaporated. The residue was slurried with aq. K_2CO_3 and then evaporated, the salts remaining being dried by azeotropic distillation with benzene and extracted several times with $CHCl_3$–acetone. The combined extracts were evaporated and cbromatographed on a column (0·8 x 8 cm) of silica gel (1·5 g) packed in benzene and eluted with benzene. Thus, fractions were obtained which showed on TLC two spots of closely similar R_f (while later fractions consisted of (TLC) unreacted compound III) and the product-component having the smaller R_f was obtained in small amount, as colorless crystals, by recrystallization from ethanol; ν_{max} 3400 (—OH), 3055, 3020, 1715 (C=O), 1640 and 880 (>C=CH_2) cm-'; m/e 426 (M^+) (63), 411 (M+-15) (10), 383 (M+-43) (13), 343 (M+-83) (13), 342 (16), 301 (M+-125) (26). 175 (12), 126 (64·5), 95 (52), 81 (56), 69 (90), 57 (54), 55 (78), 43 (77) and 41 (100). This was tentatively. identified as one of the two expected a-ketols; the two components of the crude product-mixture are probably the two a-ketols. Oxidation of the 'a-ketol' mixture (*ca. 20* mg) with bismuth trioxide (25 mg) in refluxing acetic acid (1 ml) for 1·5 hr, evaporation of the solution, and extraction of the residue with Et_2O led to a crude product which was purified by column chromatography and recyrstallization from ethanol to give a small quantity of solid, apparently consisting of two components (TLC) as indicated by a mass spectrum which had *m/e 424 (24) 422* (32), *299 (424-125) (7)* and 297 (422-125) (4). This was not further purified; it had λ_{max} 310 nm, shifting to 352 nm after the addition of two drops of 2N NaOH.

(ii) With the Sarett reagent:[13] Much the same result as in (i) was obtained. Surianol (III) (40 mg) in a solution of pyridine (2 ml) was added to a solution of Sarett reagent (43 mg, *ca. 25% excess)* in pyridine (2 ml), and after standing at room temp. for 16 hr the solution was poured into Et_2O (25 ml) which was then washed with 1N HCl followed by saturated $KHCO_3$ solution, dried ($MgSO_4$) and evaporated. The crude product contained unreacted compound III and the 'a-ketol' mixture (by TLC comparison with the products in (i)).

(iii) Jones reagent:[14] A solution of surianol (III) (25 mg) in acetone (3 ml) was stirred at room temp. during the slow dropwise addition of Jones reagent until the orange color of the reagent persisted and no compound III remained (TLC). A main component of lower R_f (0·17 after development with methanol–$CHCl_3$, 8:92; compound III having R_f 0·37 on the same chromatogram) had formed, and an i.r. spectrum of the crude product indicated carboxylic acid material. This was methylated with CH_2N_2 in Et_2O in an ice-bath, and the crude product purified on a column chromatogram (0·8 g silica gel) packed in and eluted by benzene, and finally crystallized from ethanol to give 0·5 mg, m.p. 90-100" but TLC homogeneous: $\nu_{max}^{CCl_4}$ *(0.005* M) *1735* (ester C=O) cm^{-1}; *m/e 386.3703* (M^+); calc. for $C_{31}H_{50}O_4$: 486.3709; m/e486 (M^+) (22), 471 (M+-15) (26), 361 (M^+-125) (4), 83 (43), 81 (52), 69 (100), 57 (62), 55 (72), 43 (78) and 41 (86); δ (recrystallization mother liquor) 3·57 and 3·60 (carbomethoxyl —$CH)_3$.

Oxidation of dihydrosurianol (50 mg) with Jones reagent in acetone (10 ml) at ice-bath temp. was monitored by TLC, with compound III and the a-ketol derived from III as reference standards (these having the same R_f values as the corresponding dihydro compounds). After 30 min and addition of three drops of Jones reagent most of the diiydrosurianol bad disappeared with the appearance of two components (nearly identical R_fs), with TLC R_fs the same as those of the 'a-ketol' mixture previously encountered; these disappeared on the addition of more Jones reagent, with the concomitant appearance of a very polar component (and no component with R_f higher than the a-ketol as expected for a diketone) corresponding to the diacid previously encountered. This was methylated and isolated as the diester as previously; unfortunately the quantity was insufficient for a NMR spectrum of high enough precision to provide information on the nature of the protons a to the carbonyl groups; m.p. 57–58·5°; 2 mg colorless needles.

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