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A NORLIGNAN, CRYPTORESINOL, FROM THE HEARTWOOD OF *CRYPTOMERIA JAPONICA*

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Key Word Index—*Cryptomeria japonica*, Taxodiaceae, heartwood phenol, norlignan; cryptoresinol.

Abstract—Cryptoresinol, a new norlignan has been isolated from the heartwood of *Cryptomeria japonica* and its structure was elucidated as 3,5-di(*p*-hydroxyphenyl)-2,5-epoxy-1-pentanol-3-en

INTRODUCTION

Japanese cedar (*Cryptomeria japonica* D. Don), commonly called sugi, grows well almost all over Japan. Its timber has been extensively used in the construction of Japanese houses.

We have now investigated extracts in the heartwood of *Cryptomeria japonica* Kai *et al.* [1–4] and ourselves [5] have isolated sugiresinol (**6**), hydroxysugiresinol (**7**), agatharesinol (**4**) and sequirin-C (**5**), called as norlignans (C_{17} phenolic compounds), which are regarded as useful markers for chemical taxonomy of Taxodiaceae. The isolation has been reported also of metasequirin (A and B), hydroxymetasequirin, athrotaxin, hydroxyathrotaxin, agatharesinol, sequirin (A–G) and hinokiresinol from Taxodiaceae [5–11].

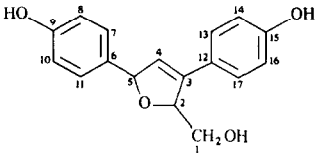
In the course of our study, we isolated a new phenolic compound which we called compound Z [5]. We now propose to name this new phenolic compound Z as cryptoresinol. We report on its structural elucidation as a new type of norlignan having the hydrofuran ring and not a pyran ring.

RESULTS AND DISCUSSION

Cryptoresinol (**1**), isolated from the methanol extractives of the heartwood of *Cryptomeria japonica* by silica gel chromatography, had the molecular formula $C_{17}H_{16}O_4$ ([M^+] at *m/z* 284). Methylation with ethereal diazomethane afforded the dimethyether derivative (mp 91–93°) which showed [M^+] at *m/z* 312 suggesting the molecular formula as $C_{19}H_{20}O_4$. Acetylation with acetic anhydride in pyridine yielded the triacetate (oil) which showed [M^+] at *m/z* 410 suggesting the molecular formula as $C_{23}H_{22}O_7$. Thus, it was proved that among the four oxygen atoms present in cryptoresinol, two were phenolic and one was an alcoholic hydroxyl group. The residual oxygen atom must exist as the ether linkage because the IR spectrum of cryptoresinol showed no carbonyl absorption band.

The ^{1}H NMR spectrum of the triacetate revealed that the signals for the protons on aromatic rings appeared as four AB type coupling groups (4 sets of 2H, *d*, $J = 8$ Hz at δ 7.02, 7.05, 7.30 and 7.41) suggesting two *p*-hydroxyphenyl structures. The UV spectrum of cryptoresinol showed λ_{max} 265 nm (log ε 4.26) indicating a double bond involved in a styryl chromophore.

In the catalytic reduction of cryptoresinol (**1**) by 5% Pd-C in a hydrogen atmosphere, the dihydro derivative (dihydrocryptoresinol (**2**)) was formed, which was different from sugiresinol (**6**) by having a pyran ring. Further catalytic reduction of the dihydro derivative finally afforded another hydrogenolysed product, which was not crystallized but it was chromatographically and spectroscopically identical with authentic dihydroagatharesinol (**3**).



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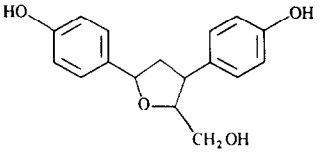

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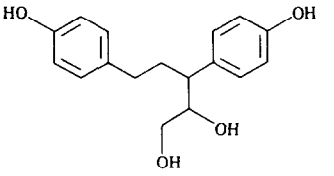

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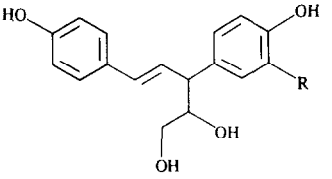

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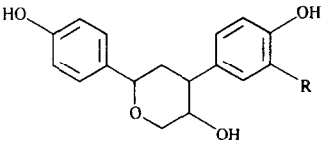
5 R = OH



6 R = H
7 R = OH

The one alcoholic hydroxyl group in cryptoresinol was primary as indicated by the ^{1}H NMR spectrum in which a large downfield shift of proton signals on acetylation was not observed (see Experimental). Thus, the secondary carbinol group in dihydroagatharesinol (**3**) must form the ether linkage The linked position should be a benzylic carbon atom (C-5) as suggested by the easy ring opening on catalytic hydrogenolysis. Thus, it was concluded that cryptoresinol was a new norlignan having a hydrofuran ring in its molecule

It was deduced that the double bond would be located at the C-4 position because the ^{1}H NMR spectrum of the triacetate, assisted by decoupling techniques, indicated the presence of two protons (δ5 68, 6.18) adjacent to an ethereal oxygen atom (epoxy ring).

Based on the above results, the structure of cryptoresinol was identified as 3,5-di(*p*-hydroxyphenyl)-2,5-epoxy-1-pentanol-3-en (**1**). The ^{13}C NMR spectrum of cryptoresinol triacetate assisted by off-resonance and decoupling techniques also supported this molecular structure.

EXPERIMENTAL

Extraction and isolation Milled heartwood of *Cryptomeria japonica* (10 kg) collected in Yamagata University Forest (Japan) was extracted with boiling MeOH The MeOH extract was concd and extracted again with *n*-hexane The insolubles were chromatographed on a column of silica gel using a mixture of C_6H_6–EtOAc–AcOH (40 20·1) as the eluting solvent. Cryptoresinol was eluted before agatharesinol and/or sequirin-C and obtained as needles (0 5 g)

Cryptoresinol (**1**) Recrystallized from Et_2O–MeOH, mp 253–255°, $[\alpha]_D^{25}$ −170 4° (MeOH, *c* 1 25), UV λ_{max}^{MeOH} nm (log ε) 265 (4 26); IR ν_{max}^{KBr} cm^{-1} 3460, 3250, 1640, 1605, 1510, 1443, 1360, 1271, 1252, 1217, 1168, 1105, 1082, 1050, 1008, 975, 918, 838, 785, 724, 690; ^{1}H NMR (60 MHz, C_5D_5N): δ4 08 (1H, *dd*, *J* = 7, 12 Hz), 4 34 (1H, *dd*, *J* = 3, 12 Hz), 5 85 (1H, *m*), 6 14 (1H, *dd*, *J* = 2, 5 Hz), 6 25 (1H, *t*, *J* = 2, 2 Hz), 7 12, 7 14, 7 45, 7 55 (each 2H, *d*, *J* = 8 Hz AB coupling in aromatic H), MS *m/z*. 284 [M$^+$]

Cryptoresinol triacetate IR ν_{max}^{KBr} cm^{-1} 1760, 1610, 1515, 1377, 1208, 1178, 1093, 1046, 1024, 922, 853, 762, ^{1}H NMR (90 MHz, $CDCl_3$) δ2 06 (3H, *s*, alcoholic OAc), 2.26, 2 28 (each 3H, *s*, phenolic OAc), 4 06 (1H, *dd*, *J* = 7, 12 Hz) and 4 51 (1H, *dd*, *J* = 3, 12 Hz) assigned to CH_2–OAc, 5.69 (1H, *m*, –O–CH), 5 95 (1H, *dd*, *J* = 2, 5 Hz, in styryl moiety), 6 18 (1H, *t*, *J* = 2, 2 Hz, benzylic H), 7.02, 7 05, 7 30, 7 41 (each 2H, *d*, *J* = 8 Hz, AB coupling in aromatic H), MS *m/z* 410 [M$^+$], 350, 308, 295, 266, 253, 237, 225, ^{13}C NMR δ66.0 (*t*, C-1), 84.1 (*d*, C-2), 129 6 (*s*, C-3), 127 1 (*d*, C-4), 87 2 (*d*, C-5), 138 1, 138 5 (each *s*, C-6, 12), 150.5, 150 7 (each *s*, C-9, 15), 121 7, 122.0 (each *d*, C-7, 11, 13, 17), 127 5, 127.8 (each *d*, C-8, 10, 14, 16), 20.9, 170 9 (*q*, *s*, OAc), 21 1, 169.2 (*q*, *s*, OAc × 2)

Cryptoresinol dimethylether. Recrystallized from C_6H_6–*n*-hexane, mp 91–93°, UV λ_{max}^{MeOH} nm (log ε) 262 (4 41), IR ν_{max}^{KBr} cm^{-1} 3440, 1640, 1610, 1580, 1515, 1460, 1350, 1300, 1258, 1192, 1175, 1097, 1072, 1038, 920, 843, ^{1}H NMR (90 MHz, $CDCl_3$). δ3 73, 3 80 (each 3H, *s*, OMe), 5.50 (1H, *m*), 5.88 (1H, *dd*, *J* = 2, 5 Hz), 6 05 (1H, *t*, *J* = 2, 2 Hz), 3 61–3 99 (2H), 6 83, 6 85, 7 26, 7 31 (each 2H, *d*, *J* = 8 Hz, AB coupling of aromatic H); MS *m/z* 312 [M$^+$]

Catalytic reduction Cryptoresinol in EtOH was shaken with 5% Pd-C catalyst in an H_2 atomosphere at room temp for 1 hr. The recovered material was subjected to prep TLC to give the hydrogenated product dihydrocryptoresinol (**2**)

Dihydrocryptoresinol (**2**). Recrystallized from Me_2CO–*n*-hexane; mp 160–164°; UV λ_{max}^{MeOH} nm (log ε): 228 (4 17), 276 (3 33) IR ν_{max}^{KBr} cm^{-1} 3475, 3290, 1608, 1592, 1514, 1439, 1382, 1215, 1172, 1120, 1083, 1018, 997, 970, 921, 882, 820, 810

Dihydrocryptoresinol triacetate. ^{1}H NMR (90 MHz, $CDCl_3$) δ2 02 (3H, *s*, alcoholic OAc), 2.28, 2.29 (each 3H, *s*, aromatic OAc), 2 20–2.35 (1H), 2.70 (1H, *ddd*, *J* = 5, 7, 12 Hz), 3 32 (1H, *ddd*, *J* = 7, 9, 12 Hz), 4 11 (1H, *dd*, *J* = 6, 12 Hz), 4 27 (1H, *dd*, *J* = 3, 12 Hz), 4 35 (1H, *ddd*, *J* = 3, 6, 12 Hz), 5.13 (1H, *dd*, *J* = 5, 10 Hz), 7 02, 7.07, 7.26, 7.48 (each 2H, *d*, *J* = 8 Hz, aromatic H)

Hydrogenolysis Further catalytic reduction of dihydrocryptoresinol under the same conditions described above afforded the hydrogenolysed product, which was identified as dihydroagatharesinol by the comparison with the authentic compound

Dihydroagathresinol Gum, IR ν_{max}^{KBr} cm^{-1} 3325, 1695, 1610, 1595, 1514, 1446, 1364, 1232, 1173, 1105, 1092, 1055, 1022, 936, 832

Acknowledgements—We are grateful to the Forestry and Forest Product Research Institute (Japan), for measurements of the MS, ^{1}H NMR and ^{13}C NMR data.

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NOVEL XANTHONES FROM *GARCINIA MANGOSTANA*, STRUCTURES OF BR-XANTHONE-A AND BR-XANTHONE-B*

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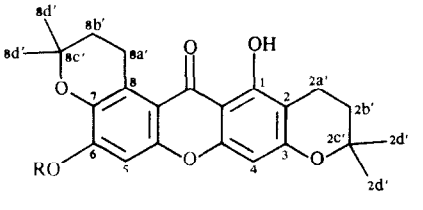
Key Word Index—*Garcinia mangostana*, Guttiferae, BR-xanthone-A, BR-xanthone-B, xanthones

Abstract—The chemical examination of the dry fruit hulls of *Garcinia mangostana* yielded, in addition to known xanthones, two new xanthones, a bis-pyrano xanthone, BR. xanthone-*A* and 1-methoxy-2,4,5-trihydroxyxanthone, BR-xanthone-B Evidence of their structures is presented

INTRODUCTION

Garcinia mangostana Linn (Guttifereae) is a tree, fairly widespread in India, Sri Lanka, Burma and known for its sweet fruits called mangosteen. In the ayurvedic system of medicine, the fruit hull of this plant finds wide application, mainly as an anti-inflammatory agent and in the treatment of diarrhoea In general, xanthones and their derivatives were shown to be effective as an allergy inhibitor and bronchodialator in treatment of asthma [1] Antileukemic xanthones have also been isolated from plants belonging to the Guttiferae family [2]. The chemistry of xanthones isolated from various plant families has been reviewed by Sultanbawa *et al.* [3]. We report now the isolation and characterization of two new xanthones from the hulls of *Garcinia mangostana*, in addition to the already reported xanthones–mangostin, gartanins and garcinones [4, 5].



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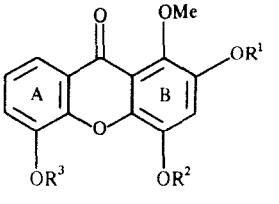
1b R = Me



2 $R^1 = R^2 = R^3 = H$
2a $R^1 = R^2 = R^3 = Me$

* Part 1 in the series 'Studies as Indigenous Medicinal Plants'